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# PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY OF THERMOPLASTIC POLYMERS

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Defence Research Establishment Atlantic

Centre de Recherches pour la Défense Atlantique

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# PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY OF THERMOPLASTIC POLYMERS

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Approved by L.J. Leggat Director/Technology Division

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## ABSTRACT

Thermal degradation mechanisms of ten thermoplastic polymers have been investigated using pyrolysis-gas chromatography with mass spectrometric and flame ionization detection. The results indicate that an unknown plastic can be identified on the basis of its degradation products and that interpretation of the degradation product analysis can be used to predict thermal degradation mechanisms and chemical structures of polymers. Identification of thermal degradation products gives insight into the hazards involved with these materials in the presence of heat and flame. Pyrograms of ten thermoplastic polymers including polyethylene (HiFax™), polymethylmethacrylate (PlexiGlas™), polyphenylene ether (Prevex™), polyacetal (Delrin™), polyamide (Nylon 6,6™), polyphenylene sulfide, polyvinylchloride (Boltaron™), polyimide (Solimide™), polyamideimide (Torlon™), and polyetheretherketone (Victrex™PEEK) obtained at 800°C and 1000°C with both flame ionization detection and quadrupole mass spectrometric detection are included.

## RESUME

Les mécanismes de dégradation thermique de dix polymères thermoplastiques ont été étudiés par pyrolyse-chromatographie en phase gazeuse avec détection par spectrométrie de masse et ionisation de flamme. Les résultats indiquent qu'un plastique inconnu peut être identifié d'après ses produits de dégradation et que l'interprétation de l'analyse des produits de dégradation peut servir à prévoir les mécanismes de dégradation thermique et la structure chimique des polymères. L'identification des produits de dégradation thermique donne un aperçu des dangers liés à ces produits en présence de chaleur et de flammes. Les dix polymères thermoplastiques dont on présente les pyrogrammes obtenus à 800°C et à 995°C avec détection par ionisation de flamme et détection par spectrométrie de masse quadripolaire sont les suivants: polyéthylène (HiFax$^{mc}$), polyméthacrylate de méthyle (Plexiglas$^{mc}$), polyphénylène-oxyde (Prevex$^{mc}$), polyacétal (Delrin$^{mc}$), polyamide (Nylon 6,6$^{mc}$), polyphénylène-sulfure, polychlorure de vinyle (Boltaron$^{mc}$), polyimide (Solimide$^{mc}$), polyamideimide (Torlon$^{mc}$) et polyétheréthercétone (Victrex$^{mc}$PEEK).

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## 1.0 INTRODUCTION

Pyrolysis-gas chromatography (pyr-GC) has been utilized in the identification of a large number of polymeric materials[1-10] including elastomers, plastics, and paints because it allows the analysis of non-volatile high molecular weight compounds with no sample pretreatment; e.g., dissolution or extraction. Samples have been pyrolyzed in several types of apparatus, and both packed and capillary gas chromatography (GC) columns have been utilized to separate the pyrolysis products. Conventional GC detectors, including the flame ionization detector (FID) and the electron capture detector (ECD), have been used to monitor the pyrolysis products which are eluted from the GC column. Typically the chromatogram of the unknown sample is compared to a library of chromatograms of various reference materials and identification of the unknown is based on the correlation of the retention times of the peaks of the unknown and a reference. To ensure that the match between the unknown and a reference material is not fortuitous, chromatograms must be acquired for the unknown and the reference standards using either two columns with different packings or at several temperatures with one column. If the chromatograms of the unknown and the reference sample are similar under these conditions, then a positive match is assumed. This procedure is very time consuming and requires the availability of a large reference library in which all chromatograms are acquired under controlled conditions.

Use of a detector that is capable of positively identifying the components of a pyrolyzed sample eliminates the need to run the chromatograms at several temperatures or on two different columns. The quadrupole mass spectrometer (MS) is such a detector. The quadrupole MS provides mass spectra of the compounds entering the detector which can be used to positively identify these compounds. In addition to this, the MS is a detector that exhibits good sensitivity for a broad range of compounds. This is in contrast to the FID and ECD, where the sensitivity is dependent upon the nature of the compound eluting from the column.

Pyrolysis GC/MS is a particularly powerful analytical tool as it can be used to identify polymeric materials on the basis of the chemical structure of

the decomposition products[11]. From the compounds produced by the pyrolysis of a material, it is possible to deduce the nature of the sample and also to study the degradation mechanism of the material. Comparison of the chromatograms of unknown materials with a library of reference chromatograms can still be used to provide confirmation of results provided the appropriate reference chromatograms are available.

This work illustrates the use of a GC/MS system for the identification of ten thermoplastic polymers and the analysis of their thermal degradation products, and shows how this knowledge can be used to deduce thermal degradation mechanisms and predict the structures of polymers. This is of particular interest because of the increasing utilization of thermoplastic materials onboard Canadian Forces ships. Thermal degradation product analysis is important for assessing the fire hazards associated with the introduction of new thermoplastic materials into ships and submarines.

## 2.0 EXPERIMENTAL APPROACH

2.1 EQUIPMENT. A Chemical Data Systems Model 170 Pyroprobe was used for all analyses and was connected to the gas chromatographs via the standard interface which was heated to 300°C. This unit has a heated coil (platinum) and was used in the pyrolysis mode (heating rate 830°C/sec). All samples were pyrolyzed in 20 mm quartz tubes for 10 seconds. Pyrolysis of the samples was carried out at two temperatures: 800°C and 1000°C.

Two gas chromatographs were utilized, a Finnigan Model 9611 and a Varian Model 4600.

The Finnigan Model 9611 was a capillary gas chromatograph, which could be used in the split (50/1), splitless or modified splitless modes and was coupled to a Finnigan MAT 5100 quadrupole MS with a SuperIncos™ data system attached. The data system contained the National Bureau of Standards library of approximately 38,000 mass spectra. The MS was run in the electron ionization (EI) mode, with an ionizing voltage of 70 eV. Table 1 shows a list of the parameters used to control the quadrupole MS detector. The data were

TABLE 1

PARAMETERS USED TO CONTROL THE QUADRUPOLE MASS SPECTROMETER

| | VALUE | RANGE |
|---|---|---|
| Electron Multiplier | -1300 volts | -3000-0 volts |
| Electrometer Range | 7 | 6-8 |
| Resolution High | +97.0 | 0-256 |
| Resolution Low | +134.0 | 0-256 |
| Ion Energy | +4.78 volts | 0-20 volts |
| Ion Program | +2.98 volts | 0-20 volts |
| Lens Voltage | -130.0 volts | -200-0 volts |
| Extractor | +2.24 volts | 0-30 volts |

acquired with a 2-second scan between 25 and 475 atomic mass units (amu). The multiple ion detection sequence used to control the data acquisition is shown diagrammatically in Figure 1.

The Varian Model 4600 utilized a FID heated at 320$^{o}$C and was controlled from a Vista 401 terminal. The unit was modified to allow pressure control of the carrier gas and was operated in the splitless mode. Nitrogen was used as a makeup gas in the FID. The makeup gas was required since the GC was designed for use with packed columns and the flow of helium from the capillary column was not large enough for efficient operation of the FID. The FID was set to a sensitivity of $10^{-9}$ amps/mV.

The temperature program used to control the GC ovens is shown in Figure 2. The ovens were kept at 40$^{o}$C for five minutes, then ramped at a rate of 10$^{o}$C/min to 300$^{o}$C.

All separations were carried out on Durabond DB-1 (100% methyl silicone, 0.25 micrometer thick bonded phase) 30m long x 0.25 mm inside diameter capillary columns. The flow rate of helium through the column was kept at approximately 1.5 mL/min under pressure control conditions.

2.2 MATERIALS. The thermoplastics examined in this study are listed in Table 2. This table includes the commercial and chemical names as well as the physical nature of the various thermoplastics. The melting points of the crystalline thermoplastics or glass transition temperatures of amorphous thermoplastic materials are also listed in Table 2. The general structures of these materials are shown in Table 3.

TABLE 2

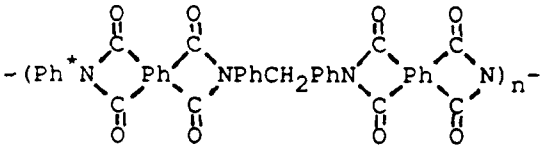
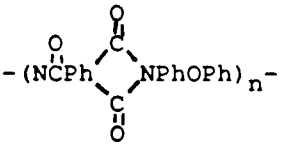
TEN THERMOPLASTIC POLYMERS USED IN THIS STUDY

| Commercial Name | Chemical Name | Physical State | Melting Point (°C) |
|---|---|---|---|
| Hifax™ | Polyethylene | White block | 156 |
| PPS | Polyphenylene sulfide | Beige powder | 282 |
| Prevex VQA™ | Polyphenylene ether | Cream pellets | 211 |
| Victrex PEEK™ | Polyetheretherketone | Beige granules | 342 |
| Nylon 6,6™ | Polyamide | White block | 261 |
| Plexiglas™ | Polymethylmethacrylate | Transparent block | 90-100* |
| Delrin™ | Polyacetal | White block | 179 |
| Torlon™ | Polyamideimide | Brown stick | 275* |
| Boltaron™ | Polyvinylchloride | Grey block | 75-105* |
| Solimide | Polyimide | Yellow foam | 310-365* |

*Glass transition temperature ($T_g$). These materials are amorphous.

**Table 3**

Chemical structures of the ten thermoplastic polymers studied.

| | |
|---|---|
| Polyethylene | $-(CH_2CH_2)_n-$ |
| Polyvinylchloride | $-(CH_2CHCl)_n-$ |
| Polyacetal | $-(CH_2O)_n-$ |
| Polymethylmethacrylate | $-(CH_2\overset{CH_3}{\overset{\vert}{C}})_n-$ with $CO_2CH_3$ |
| Polyamide (Nylon 6,6) | $-(NH(CH_2)_4NHC(CH_2)_4C)_n-$ |
| Polyphenylene sulfide | $-(PhS)_n-$ |
| Polyphenylene ether | $-(PhO)_n-$ |
| Polyimide[1] |  |
| Polyetheretherketone[1] | $-(OPhCPhOPhOPh)_n-$ |
| Polyamideimide[1] |  |

[1] - The exact structure of these thermoplastics was not known. The structure provided is characteristic of that general class of plastic.

Ph - benzene ring

Ph* - pyridine

2.3 PROCEDURE. Representative samples of the various plastics were taken from the interior of the plastic blocks to minimize the possibility of inhomogeneity caused by environmental surface degradation. The difference in the nature (pellets, sheet, foam and powder) of the polymers made it impossible to obtain samples with a constant geometry. Although the sample size was not the main concern in this experiment, it was essential to have enough sample to obtain a good response and at the same time avoid overloading the capillary column. A sample of approximately one milligram was determined to give a good chromatogram.

## 3.0 RESULTS AND DISCUSSION

Chromatograms of a polymer obtained following the pyrolysis of a sample are called pyrograms. The pyrograms of the ten thermoplastic materials listed in Table 2 obtained using flame ionization detection and quadrupole mass spectrometric detection are shown in Figures 3-6 and Figures 9 through 44. Appendix A lists the major pyrolysis products of each polymer.

3.1 THERMAL DEGRADATION MECHANISMS. Thermoplastic materials are known to thermally degrade by four major mechanisms[1,11-13]. These four mechanisms are (1) depolymerization, (2) random chain scission, (3) cleavage of side groups and (4) interchain condensation.

Depolymerization is also known as 'unzippering' and generally proceeds by the removal of monomer units from the end of the polymer chain, but can also initiate from any weak bond in the polymer chain. This degradation mechanism is characteristic of some common plastics including polymethylmethacrylate, poly-α-methylstyrene and polyoxymethylene[13].

Random chain scission is a statistical polymer chain break and produces relatively high molecular weight fragments. This can be followed by (a) depolymerization from radical ends, (b) disproportionation, or (c) cyclization. Mechanism (a) is characteristic of polystyrene, (b) of polyethylene, and (c) of polydimethylsiloxane[13].

Cleavage of side groups is followed by cyclization and fragmentation of the polymer to form aromatics. Besides the products formed by cyclization and fragmentation, monomers and main chain fragmentation products are also obtained. This type of degradation is characteristic of polyvinylchloride and polyacrylonitrile which release HCl and HCN, respectively[13].

Interchain condensation is often accompanied by the release of small molecules and is followed by the formation of carbonaceous residues. High temperature polymers such as phenol-formaldehyde resins and polyimides degrade this way[13].

3.2 REPRODUCIBILITY. Several factors influence the reproducibility of pyrograms including the geometry and homogeneity of the sample, variation in the actual temperature of the pyroprobe at a particular temperature setting and the rate of temperature rise, flow variations through the column and catalytic reactions on the platinum heating coil[1,4,14].

The heating rate and pyrolysis temperature are especially important factors because the rate of temperature rise in the pyroprobe and the final pyrolysis temperature are assumed to be controlled. However, the non-reproducibility of results among different laboratories seems to be related to variations in the final pyrolysis temperature[14]. Even though the same heating rate and temperature maximum are utilized, the actual heating rates and final temperatures vary from one piece of equipment to another.

Tar, produced during the pyrolysis of polymers, has been observed to contaminate GC columns[15] and affect the results obtained from pyrolysis studies of polymers. Variations in the sensitivity of the MS detector can also affect reproducibility of pyrolysis fingerprint patterns.

In this work, care was taken to ensure that experimental conditions were kept as constant as possible so that the same sample could be shown to yield reproducible qualitative results.

3.3 THERMOPLASTIC PYROGRAMS. In the following section, the pyrograms produced by the thermal degradation of each of the ten thermoplastics are discussed separately. The discussion involves an analysis of the pyrograms obtained at 800°C and 1000°C with particular emphasis on the nature of the degradation products. The nature of the products is used to either deduce the degradation mechanism of a polymer or confirm the degradation mechanism found in the literature for a particular polymer. The retention time (RT) of a peak is denoted in minutes for the pyrograms obtained with FID and by scan number for the pyrograms obtained with MS detection. Scans of 2-second duration were used in the acquisition of the pyrograms with MS detection and therefore the RT in minutes of a peak listed by scan number can be calculated by multiplying the scan number by 2 and dividing by 60; e.g., a peak at scan 60 has a retention time of 2 minutes. When a peak or compound is listed as scan 100/101, for example, then the first scan number, i.e. 100 in this case, refers to the pyrolysis at 1000°C, while the second scan number, i.e. 101 in this case, refers to the pyrolysis at 800°C.

3.3.1 Polyethylene (PE). PE has been shown to thermally degrade by a random chain scission mechanism which is followed by radical transfer and disproportionation[6,12]. This results in the polymer chain breaking at any point along its length. An initial rapid reduction in the molecular weight is observed which slows as the degradation progresses.

The pyrolysis of PE (Hifax™) yields pyrograms with very characteristic patterns (Figures 3 through 6). The pyrograms consist of a number of three peak groupings with retention times between 10 and 30 minutes. In the interest of convenience, these three peak groups will be called 'triplets' in this document. For example, in Figure 7 the three peaks centered at scan 553 were determined to be a diene, an alkene and an alkane from their mass spectra (scan 547 was found to be pentadecadiene, scan 553 was pentadecene and scan 557 was pentadecane). Such a sequence is repeated for each triplet corresponding to different carbon homologs; i.e., hydrocarbons containing the same number of carbon atoms but varying degrees of saturation. The alkene is always the most intense peak of the triplet and the alkane is the least intense.

The thermal degradation of PE by pyrolysis-GC has been studied by Wampler and Levy[6]. They found that for each triplet corresponding to a particular carbon homolog the intensity of the alkane peak decreased while the intensity of the diene peak increased as the pyrolysis temperature was increased. This variation of intensity with temperature was difficult to observe in the pyrograms shown in Figures 3 and 4 and Figures 5 and 6, respectively, but was evident in the expanded pyrograms obtained with MS detection shown in Figures 7 and 8. For instance, in Figure 7, which shows the pyrogram of PE obtained at 1000°C, the intensity of the first peak of the triplet (the diene) centered at scan 513 is more intense than the third peak of the triplet (the alkane) while in Figure 8, which shows the pyrogram of PE obtained at 800°C, the first peak of the triplet (the diene) centered at scan 508 has approximately the same intensity as the third peak (the alkane). It should be noted that these triplets correspond to the same carbon homolog. Wampler and Levy[6] also observed that the larger the number of carbons found in the compounds that make up the triplet the closer the intensity of the diene peak is to the intensity of the alkene peak. This trend was not observed in this study. Further, they observed that the relative intensity of the diene peak compared to the alkane and alkene peaks was greater at 1000°C than at 800°C. This was also observed in this work and is illustrated in Figures 7 and 8. This was explained[6] by the fact that at higher temperatures more secondary reactions such as dehydrogenation occur which produce more dienes.

3.3.2 Polymethylmethacrylate (PMMA). It is known that PMMA thermally degrades by a depolymerization mechanism which results in the production of the monomer unit[13]. The monomer (methylmethacrylate) would then be expected to give rise to the major peak in the pyrogram of PMMA.

Uncomplicated patterns were obtained from the pyrolysis of PMMA at both 1000°C and 800°C. The pyrograms obtained with FID (Figures 9 and 10) show a single peak at 1.5 minutes RT followed by two very intense peaks between 3 and 4 minutes RT. The pyrograms obtained at 1000°C and 800°C with MS detection are shown in Figures 11 and 12. At 1000°C, only one peak at scan 97 was observed in the pyrogram while at 800°C the pyrogram had two peaks at scans 90 and 164.

The major peak in the pyrograms shown in Figures 11 and 12 was determined on the basis of its mass spectrum to be the methyl ester of 2-methyl-2-propenoic acid which is methylmethacrylate, the monomer unit. The other peak observed in the pyrogram obtained at 800°C corresponded to the methyl ester of cyclopropanecarboxylic acid. This compound could have been formed by way of a secondary reaction such as cyclization of methylmethacrylate which is more likely to occur at lower temperatures.

The two adjacent peaks (RT 3-4 minutes) in the pyrograms acquired with FID are probably the monomer unit. The split peak may have resulted from inefficient transfer of the pyrolysate from the pyroprobe to the capillary column resulting in a broad peak.

3.3.3 Polyphenylene Ether (PPE). PPE, also known as polyphenylene oxide, is reported to thermally degrade by a random chain scission mechanism[16,17]. The pyrograms of PPE obtained with a flame ionization detection are shown in Figures 13 and 14. The major peaks are concentrated in three retention time windows: between 5 and 13 minutes RT, between 19 and 23 minutes RT and at 27 minutes RT.

Although the peaks observed in the pyrograms obtained with MS detection (Figures 15 and 16) are located in the same time windows as those obtained with FID, fewer peaks are found. The pyrograms generated at 1000°C and 800°C using MS detection are similar in that they contain peaks with the same retention times, but the relative intensities of the peaks vary from one pyrogram to the other.

Two of the most intense peaks in the pyrograms were found to correspond to styrene (scan 235/234) and the triphenyl ester of phosphoric acid (scan 818/823). PPE formulations often contain styrene or substituted styrene as a cross-linking agent to confer more flexibility[18]. Both styrene and 1-methylethenylbenzene or methylstyrene (scan 291/290) were degradation products found in the pyrogram of PPE. The triphenyl ester of phosphoric acid has been used as a plasticizer and can have fire-retardant properties.

Phosphorus containing flame retardants are thought to act mainly in the condensed phase by interrupting the reactions that result in degradation of a polymeric material[19]. Phosphate esters are thermally degraded to form phosphoric acid which promotes dehydration and charring of the polymer. The carbonaceous layer formed is protected by a glassy phosphorus-based coating that shields the polymer from oxygen attack and radiant heat. However, there is also evidence that some phosphorus-based flame retardants are effective in the gas phase[19]. The grade of PPE used in this study (Prevex™ VQA) is reported by the manufacturer to contain a flame retardant.

Other peaks in the pyrogram were determined to be 2-methylphenol (scan 333/332), 2,5-dimethylphenol (scan 359/360) and 2,5,6-trimethylphenol (scan 409/411). As PPE is formed by a stepwise or condensation polymerization reaction of methyl substituted phenols, these fragments suggest that this particular PPE was produced from a mixture of these monomers and degrades by a random chain scission mechanism. Condensation polymerization refers to a reaction between two molecules to produce a larger molecule. Often a small molecule, such as water, is released as the reaction proceeds in a stepwise fashion to yield a polymer.

3.3.4 Polyacetal. Figures 17 and 18 show the pyrograms of polyacetal obtained with FID at 1000°C and 800°C, respectively. The pyrograms are characterized by two peaks with retention times between 1.5 and 2 minutes.

Figures 19 and 20 show the pyrograms acquired with MS detection at 1000°C and 800°C, respectively. These pyrograms are characterized by a single peak at scan 47/45. Analysis of the mass spectra of the compound giving rise to this peak in each pyrogram indicates that it is formaldehyde.

The presence of a single pyrolysis product suggests that polyacetal degrades by a depolymerization mechanism, in a matter similar to PMMA, and this has been noted in the literature[13], although random chain scission followed by depolymerization from the radical chain ends has also been proposed as a mechanism[11]. It is presumed that both peaks detected with FID are the same compound and result from inefficient transfer of the pyrolysate from the pyroprobe to the capillary column.

3.3.5 Polyamide (Nylon 6, 6™). The thermal degradation of aliphatic polyamides has been reported to proceed by a random chain scission mechanism which begins with the production of $CO_2$ and $H_2O$ and is followed by the hydrolysis of the amide bond[2,3]. It has also been reported that some cyclization occurs and secondary reactions involving the homolytic cleavage of C-C, C-N and C-H bonds takes place. The presence of moisture has been reported to greatly complicate the degradation of polyamides such as Nylon 6,6™ [11]. The concentration of secondary reaction products has been observed to increase as the pyrolysis temperature is increased.

The pyrograms of the Nylon 6,6™ (polyhexamethylene adipamide) obtained at 1000°C and 800°C with FID are shown in Figures 21 and 22, while those obtained with MS detection are shown in Figures 23 and 24.

The pyrograms obtained with FID are similar in that both have major peaks with retention times less than two minutes and peaks with retention times at 5.2 minutes. However, the pyrogram obtained at 1000°C has a peak at 2.9 minutes while that obtained at 800°C has two peaks with retention times of 6.4 and 6.8 minutes, respectively.

The pyrograms shown in Figures 23 and 24 have two major peaks at scan (43/43) and scan (130/142). On the basis of the mass spectra, the peak at scan (43/43) was determined to be a mixture of $CO_2$ and propane. The peak at scan (130/142) was found to be cyclopentanone which is a degradation product that is characteristic of nylons prepared from the condensation of a diamine with hexanedioic acid, such as Nylon 6,6[3]. Although this is a degradation product which is characteristic of Nylon 6,6™, it is difficult to confirm the degradation mechanism of Nylon 6,6™ on the basis of the degradation products identified from the pyrograms.

3.3.6 Polyphenylene Sulfide (PPS). Polythioethers such as PPS are reported to thermally degrade by a random chain scission mechanism[16,17]. The pyrograms of PPS at 1000°C and 800°C obtained with FID and MS detection are shown in Figures 25 and 26 and Figures 27 and 28, respectively. The pyrograms obtained show similar patterns of peaks at both pyrolysis temperatures

for a particular detector, although the relative intensity of the peaks in pyrograms generated with MS detection differ from those in the corresponding pyrograms generated with FID. This may result from the different sensitivities of the FID and MS detectors for particular compounds, which, in turn, affects the relative intensities of the peaks in the pyrograms acquired with a particular detector.

The major compounds produced by the pyrolysis of PPS were found to be $SO_2$ (scan 47/48), benzene (scan 74/78), benzenethiol (scan 254/259), biphenyl (scan 481/489), 1,1'-thiobisbenzene (scan 562/562), dibenzothiophene (scan 623/628), S-phenyl ester of benzenesulfinothioc acid (scan 647/646) and 1,4-di(thiophenyl)benzene (scan 859/858). The presence of benzene, benzenethiol, 1,1'-thiobisbenzene and 1,4-di(thiophenyl)benzene confirm that PPS degrades by a random chain scission mechanism. This is probably followed by secondary reactions, including condensation reactions, to form compounds such as biphenyl and dibenzothiophene.

3.3.7 Polyvinylchloride (PVC). The thermal degradation of PVC is reported to proceed by the cleavage of side groups and the subsequent release of small molecules, in this case hydrogen chloride, to form polyenes which then undergo cyclization to form aromatics[13]. It has been noted that at higher temperatures the free radical depolymerization mechanism becomes more important[5], although elimination of small molecules occurs simultaneously. The relative importance of these competing mechanisms depends on the pyrolysis temperature.

The pyrograms of polyvinyl chloride obtained with FID and MS detection are shown in Figures 29 and 30 and Figures 31 and 32, respecti...,.

The major peaks in Figures 31 and 32 were found to be HCl (scan 48/48), benzene (scan 83/85), methylmethacrylate (scan 106/103), toluene (scan 136/138), ethyl benzene (scan 209/212), bicyclo [4.2.0]octa-1,3,5-triene (scan 224/228), 1-propynylbenzene (scan 322/326), and 1-methylene-1H-indene (scan 396/400). Degradation products of this type are expected since the major pyrolysis products of PVC have been shown to be benzene, olefins and

aromatics[10]. These products confirm that PVC degrades by the release of HCl and the formation of polyenes and subsequent cyclization.

3.3.8 Polyimide (PI). Interchain condensation with loss of small molecules is thought to be the mechanism of thermal degradation of polyimides[19]. Solimide™ is a fully aromatic polyimide formed by the condensation of benzenetetracarboxylic acid dianhydride with a mixture of aromatic and heteroaromatic diamines (methylene dianiline and diaminopyridine).

The pyrograms of PI obtained with FID are shown in Figures 33 and 34 while the pyrograms obtained with MS detection are shown in Figures 35 and 36.

The major peaks in the pyrograms obtained with MS detection at 1000°C and 800°C were carbon dioxide (scan 46/45), benzene (scan 80/77), toluene (scan 135/134), and bicyclo[4.2.0]octa-1,3,5-triene (scan 222/219). The pyrogram at 1000°C contained a number of other peaks including benzonitrile (scan 274), methylbenzonitrile (scans 324, 335), methylaniline (scan 330), isocyano-4-methylbenzene (scan 342), naphthalene (scan 391), benzenedicarbonitrile (scan 436), 1,1'-biphenyl (scan 480), methyl-1,1'-biphenyl (scan 500), 9H-fluorene (scan 561), benzo[H]quinoline (scan 599) and benzo[C]cinnoline (scan 614).

These pyrolysis products confirm the mechanism of degradation proposed in the literature[19]; i.e., the release of small molecules such as $CO_2$, benzene, toluene, methylaniline, isocyano-4-methylbenzene and benzonitriles and the formation of higher molecular weight compounds, such as biphenyl, benzo[H]quinoline and benzo[C]cinnoline, from condensation reactions.

3.3.9 Polyamideimide (Torlon™). As a result of the chemical linkages formed in the synthesis of a polyamideimide; i.e., amide and imide bonds, Torlon™ might be expected to thermally degrade in a manner similar to aromatic polyamides and polyimides[19]. That is, degradation would involve the release of small molecules followed by condensation and the release of higher molecular weight compounds.

The pyrograms of Torlon™ obtained with FID at 1000°C and 800°C are shown in Figures 37 and 38, respectively, while those obtained with MS detection are shown in Figures 39 and 40. Some of the major peaks in the pyrograms obtained using MS detection were determined to be carbon dioxide (scan 44/42), benzene (scan 78/79), aniline (scan 270/268), phenol (scan 280/282), methylaniline (scan 327/325), 1H-isoindole-1,3(2H)-dione (scan 500/500), 4-phenoxyaniline (scan 611/608), 2-phenyl-1H-isoindole-1,3(2H)-dione (scan 703/700) and 3,5-diphenyl-1,3,4-oxadiazol-2(3H)-one (scan 809/806).

The exact structure of Torlon™ is not available. However, an example of a polyamideimide is shown in Table 3. The presence of $CO_2$, benzene, and aniline suggest that Torlon™ does degrade by release of small molecules which is followed by condensation reactions that produce compounds such as 3,5-diphenyl-1,3,4-oxadiazol-2(3H)-one.

3.3.10 Polyetheretherketone (PEEK). The pyrograms of PEEK obtained using FID are shown in Figures 41 and 42. There is one major peak at approximately 10 minutes RT. The pyrograms obtained with MS detection are shown in Figures 43 and 44. The major peaks were found to be: $CO_2$ (scan 43), benzene (scan 76), toluene (scan 127), 2,5-cyclohexadiene-2,4-dione (scan 220), phenol (scan 281), 1,1'-oxybisbenzene (scan 483), dibenzofuran (scan 531), diphenylmethanone (scan 568), 4-phenoxyphenol (scan 602) and 1,4-diphenoxybenzene (scan 748).

The actual chemical structure of this polymer is not available. However, it is known that PEEK is a fully aromatic compound containing ketone and ether linkages between aromatic rings in the polymer chain. The pyrolysis products found are representative of an aromatic structure and indicate degradation by a random chain scission mechanism. The chain scission is followed by loss of carbon dioxide and condensation reactions.

3.4 ADVANTAGES OF PYROLYSIS GC/MS. One of the most apparent advantages of the pyrolysis GC with MS detection is the universality of the MS detector compared to detectors such as FID and ECD. Unlike the FID or ECD, which have high sensitivity for certain types of compounds, the MS detector detects all

compounds that produce ions in the mass range that is scanned. For instance, the FID has high sensitivity for hydrocarbons, but has very low sensitivity for gases such as $SO_2$, $CO_2$, and CO, while the MS detector has good sensitivity for both hydrocarbons and gases and gives a more realistic indication of the degradation products produced by the various plastics.

In addition to identifying polymeric materials on the basis of characteristic fragments formed during pyrolysis, pyrolysis GC/MS can also be utilized to distinguish between plastics with the same basic structure but with differing additive packages such as flame retardants, plasticizers and smoke inhibitors. For example, the PPE sample used in this study (Prevex™ VQA) was known to contain a flame retardant (Figures 15 and 16), and this was found to be the triphenyl ester of phosphoric acid.

The identification of pyrolysis products also allows the study of the degradation mechanisms of a particular plastic. For example, the structures of both PPE and PPS were known (see Table 3), but little was known about their degradation mechanisms. Based on the fragments produced during the pyrolysis of these polymers, it was concluded that random chain scission was a major degradation mechanism for both. In random chain scission, the polymer can break at any point along the chain. As a result of the stability of the benzene ring, the bonds that break are the ether (-O-) bonds in PPE or thio-ether (-S-) bonds in PPS. Substituted phenols and benzene thiols were observed in the pyrograms for PPE and PPS, respectively, and these compounds would be produced if the polymer chain was cleaved at the ether or thio-ether bond.

The exact structures of PEEK and Torlon™ (polyamideimide) were not known and could not be obtained from the manufacturers. The chemicals used to synthesize these polymers was also proprietary information. However, knowledge of the types of chemical bonds along the polymer backbone and the information gained from the mass spectral identification of the fragments produced following pyrolysis of these plastics were used to predict their structure. For instance, PEEK (polyetheretherketone) should have both etherether (R-O-R'-O-R") and ketone (R-C(O)-R') linkages, where R, R' and R"

are aromatic rings and C(O) is a carbonyl group. Benzene (Ph), phenol (PhOH), 1,1'-oxybisbenzene (PhOPh), 4-phenoxyphenol (PhOPhOH), and 1,4-diphenoxybenzene (PhOPhOPh), which are all found in the pyrogram of PEEK, are fragments characteristic of a polymer containing the segment -PhOPhOPh- which is an etherether functionality and are all found in the pyrogram of PEEK. Diphenylmethanone (PhC(O)Ph) is also found in the pyrolysis products and contains a ketone functionality. A possible structure for PEEK which incorporates these fragments and is wholly aromatic is given in Table 3.

Torlon™ contains both amide (-C(O)NH-) and imide (-C(O)NRC(O)-) functionalities. An amide is formed from the reaction of a carboxylic acid (RCOOH) and an amine ($RNH_2$), while imides are formed when an amine reacts with a dicarboxylic acid or acid anhydride. Amines such as aniline, methylaniline, benzenediamine, and phenoxyaniline were observed as products of the degradation of Torlon™. Also, isoindoledione (phthalimide) and N-phenyl-isoindoledione, which are condensation products of phthalic acid or phthalic anhydride and an amine were found. On the basis of these products, a possible structure for Torlon is shown in Table 3. This polymer could be prepared by the condensation of an aromatic diamine, such as benzenediamine ($NH_2PhNH_2$) or 1,1'-oxybis(4-aminobenzene) ($NH_2PhOPhNH_2$), and a benzenetricarboxylic acid, such as 1,2,4- or 1,2,5-benzenetricarboxylic acid. An amine functionality reacting with the carboxylic acid groups ortho to each other would give an imide linkage while the reaction of an amine with the carboxylic acid group para to the 1 or 5 position would yield an amide linkage.

The effect of varying pyrolysis temperature or pyrolysis time on degradation can also be studied through the fragments formed during pyrolysis. In general, the higher the pyrolysis temperature the more complete the degradation of the polymer. For instance, the pyrogram generated for a polymer by a depolymerization mechanism should contain fewer peaks as the pyrolysis temperature is increased; i.e., more monomeric material and less dimer, trimer, and so on should be produced[7]. This is observed in the pyrograms of PMMA generated at 1000°C and 800°C. There is only one major peak in the pyrogram at 1000°C, but a second in the pyrogram at 800°C.

3.5 TOXICITY OF THERMAL DEGRADATION PRODUCTS. At a high enough temperature, all organic materials will thermally degrade. In the presence of oxygen, the products of the complete thermal degradation of hydrocarbon-based polymers are predictable; i.e., carbon monoxide, carbon dioxide and water. If heteroatoms such as nitrogen and sulfur are present in the polymer, oxides of sulfur and nitrogen will also be formed. In most instances, the conditions required for the complete combustion alluded to above are not realized, and the thermal degradation products are less easily predicted. Further, the presence of halogens, phosphorus-based compounds and other additives increase the number and type of degradation products formed by a particular plastic.

Toxic and hazardous volatiles were produced by a majority of the plastics tested. Some of these are listed in Table 4 along with time weighted average threshold limit values (TWA-TLV)[21] for those compounds that have such published limits. Information about the nature of the degradation products of thermoplastics gives insight into the thermal degradation mechanisms of the various plastics and the types of volatiles that would be released when these plastics are exposed to a thermal stress. This is important in the assessment of a plastic for shipboard use as the compounds produced may have an effect on crewmen and equipment far removed from any actual fire.

TABLE 4

TIME WEIGHTED AVERAGE THRESHOLD LIMIT VALUES (TWA-TLV) AND THE SHORT EXPOSURE LIMIT (STEL) OF SOME DEGRADATION PRODUCTS OF THERMOPLASTICS

| COMPOUND | TLV-TWA[1] | TLV-STEL[2] |
|---|---|---|
| $CO_2$ | 5000 | 30,000 |
| CO | 50 | 400 |
| benzene | 10 | 25 |
| toluene | 100 | 150 |
| ethylbenzene | 100 | 125 |
| styrene | 50 | 100 |
| phenol (skin) | 5 | 10 |
| $SO_2$ | 2 | 5 |
| HCl | 5 | -- |
| methylmethacrylate | 100 | 125 |
| aniline | 2 | -- |
| formaldehyde | 1 | 2 |
| biphenyl | 0.2 | 0.6 |

1. The time weighted average concentration for a normal 8-hour day and a 40-hour work week to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

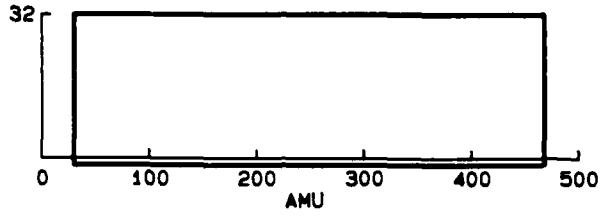
2. The concentration to which workers can be exposed continuously for short periods of time without suffering from irritation, chronic or irreversible tissue damage, or narcosis of sufficient degree to increase the likelihood of accidental injury or reduce work efficiency.

## 4.0 CONCLUSIONS

A library of pyrograms of ten thermoplastic materials has been prepared. The thermoplastics were pyrolyzed at both 1000°C and 800°C, and both flame ionization and mass spectrometric detectors were utilized to record the pyrograms. These pyrograms can be used to identify unknown thermoplastics by matching the chromatographic pattern of an unknown with those contained in the library.

It has been shown that pyrolysis GC/MS is capable of identifying polymeric materials on the basis of the fragments formed during pyrolysis. The ability of the mass spectrometer to identify pyrolysis products has been utilized to study the degradation mechanisms of plastics, to predict the chemical structure of plastics where they are not known, and to comment on the toxicity and hazards involved with the use of a particular plastic in a fire situation.

| | |
|---|---|
| MASS DEFECT AT 100 U | 30 MMU |
| MASTER RATE | 32 |
| TOTAL ACQU TIME | 1.867 s |
| TOTAL SCAN TIME | 2.000 s |
| CENT SAMP INT | 0.200 ms |
| CALI MASS RANGE | 69 TO 614 U |

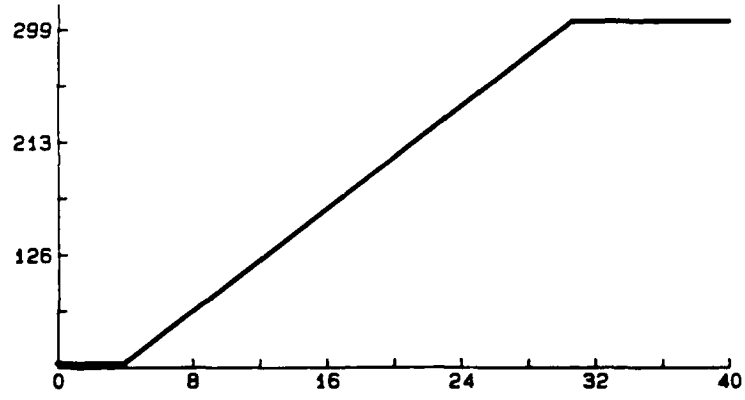



| INT # | BEGIN MASS | END MASS | TIME REQUEST | (s) ACTUAL | MPW | MFW | MA | TH | BL | ION |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 24.507 | 475.642 | 1.000 | 2.000 | 1 | 80 | 0 | 1 | 0 | POS |
| 1. | 24.507 | 475.642 | 2.000 | 1.867 | 3 | 80 | 10 | 1 | 0 | POS |

FIGURE 1: The Multiple Ion Detection (MID) sequence used to acquire the quadrupole MS of the various thermoplastics. The quadrupole MS scanned all masses from 25 to 475 atomic mass units (amu) in 2 seconds.

GC VALVES:

| | CLOSE | OPEN |
|---|---|---|
| (CV) CAPILLARY | 0.0 | 40.0 |
| (DV) DIVERT | 0.0 | 40.0 |




| SEG.# | FROM TEMP (C) | | TO TEMP (C) | RATE (C/m) | TIME (min) | TOTAL TIME (min) |
|---|---|---|---|---|---|---|
| 1 | 40 | - | 40 | - | 4.0 | 4.0 |
| 2 | 40 | - | 300 | 10.0 | 26.0 | 30.0 |
| 3 | 300 | - | 300 | - | 10.0 | 40.0 |

FIGURE 2: Temperature program used to control the Varian 4600 and Finnigan 9611 GC ovens.

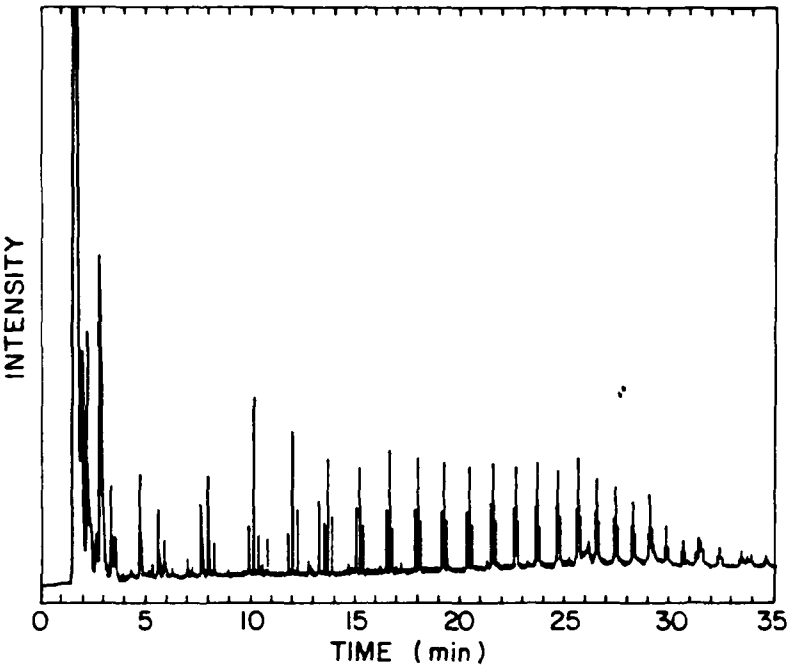



FIGURE 3: Pyrogram of polyethylene at 1000°C (flame ionization detection).

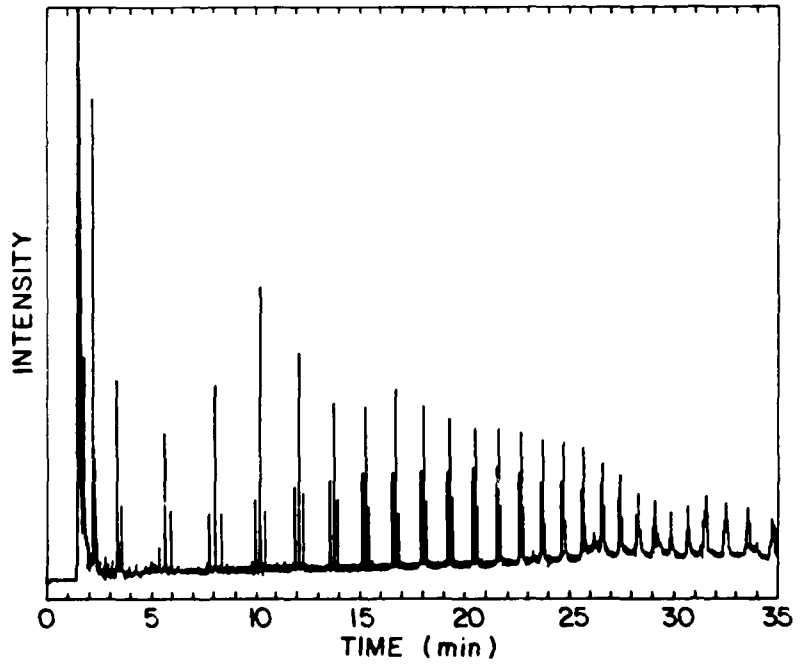



FIGURE 4: Pyrogram of polyethylene at 800°C (flame ionization detection).

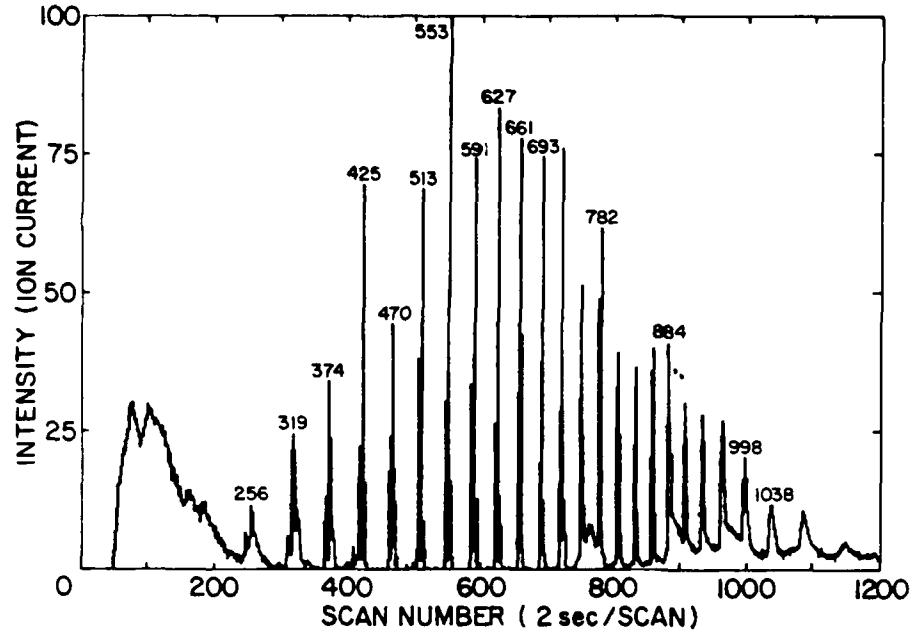



FIGURE 5: Pyrogram of polyethylene at 1000°C (mass spectrometric detection).

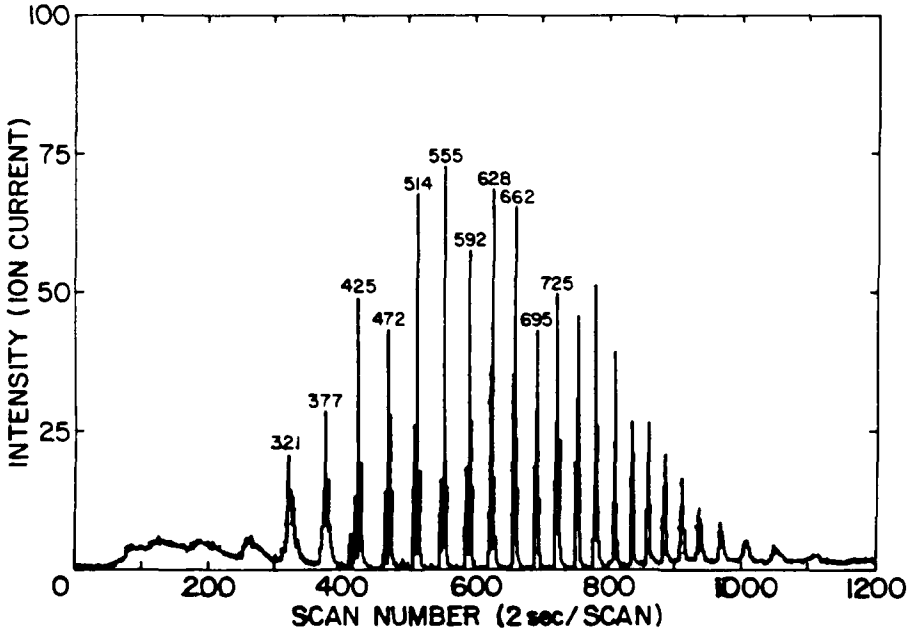



FIGURE 6: Pyrogram of polyethylene at 800°C (mass spectrometric detection).

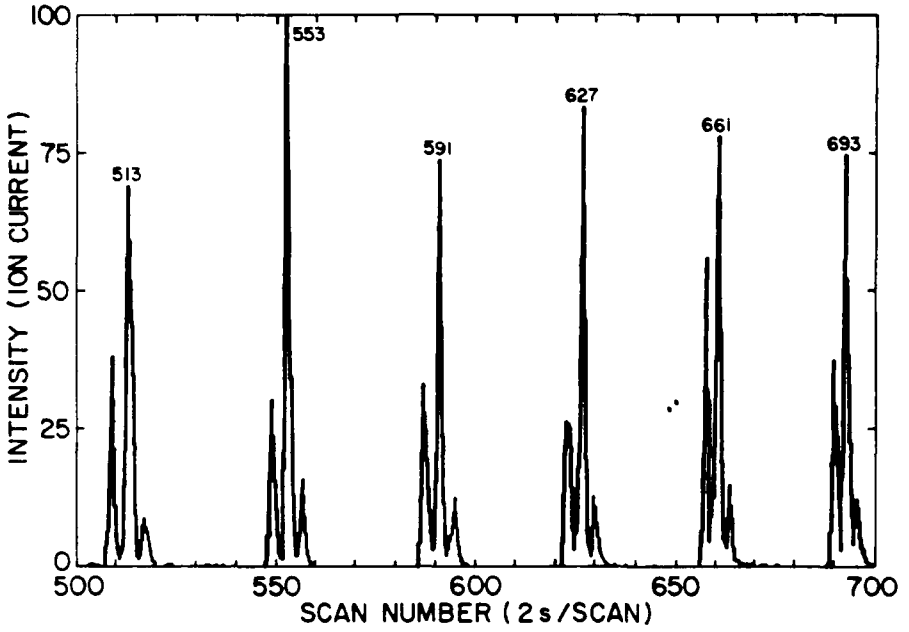



FIGURE 7: 'Triplet' patterns from pyrogram of polyethylene at 1000°C. Scans 500 to 700 are shown and the expanded scale shows 'triplets' plainly (mass spectrometric detection).

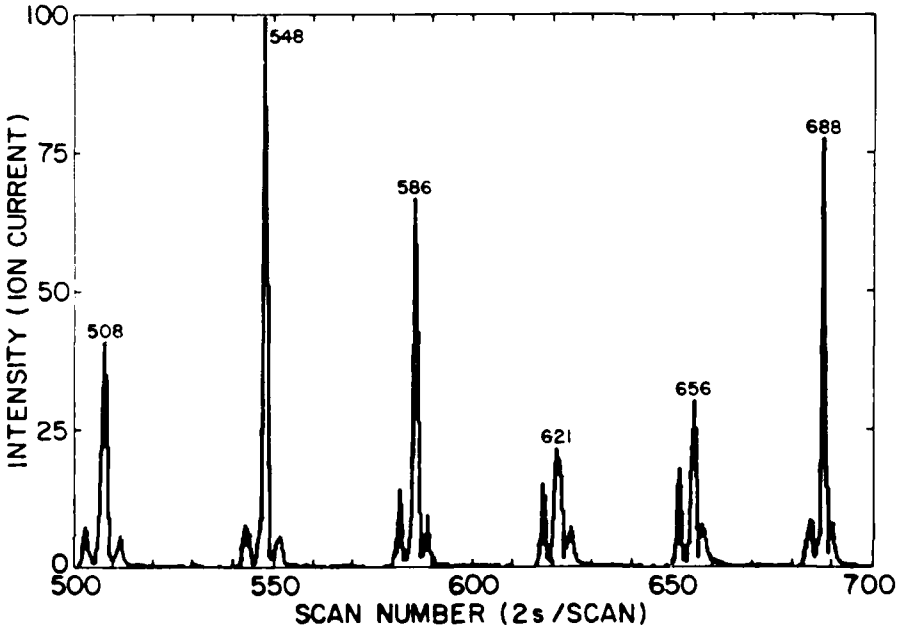



FIGURE 8: 'Triplet' patterns from pyrogram of polyethylene at 800°C (mass spectrometric detection).

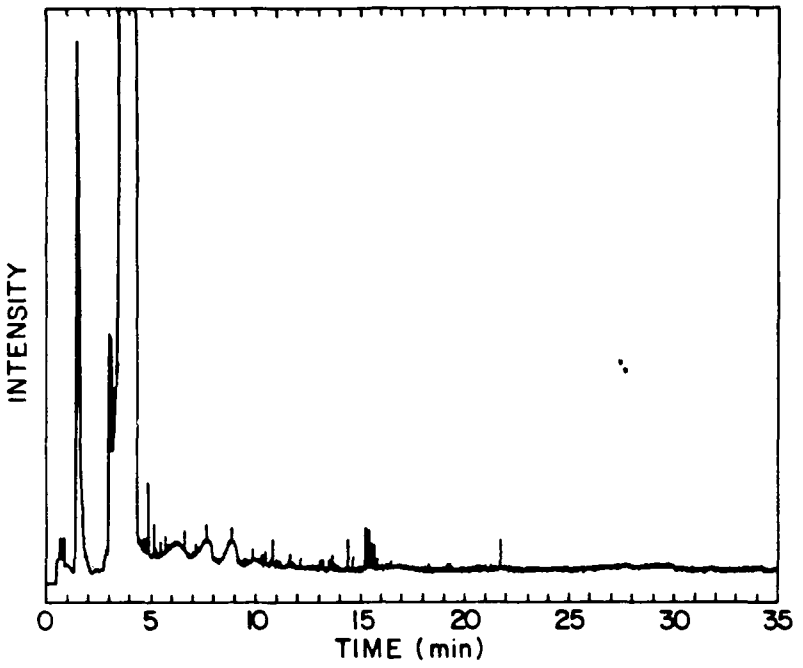



FIGURE 9: Pyrogram of polymethylmethacrylate at 1000°C (flame ionization detection).

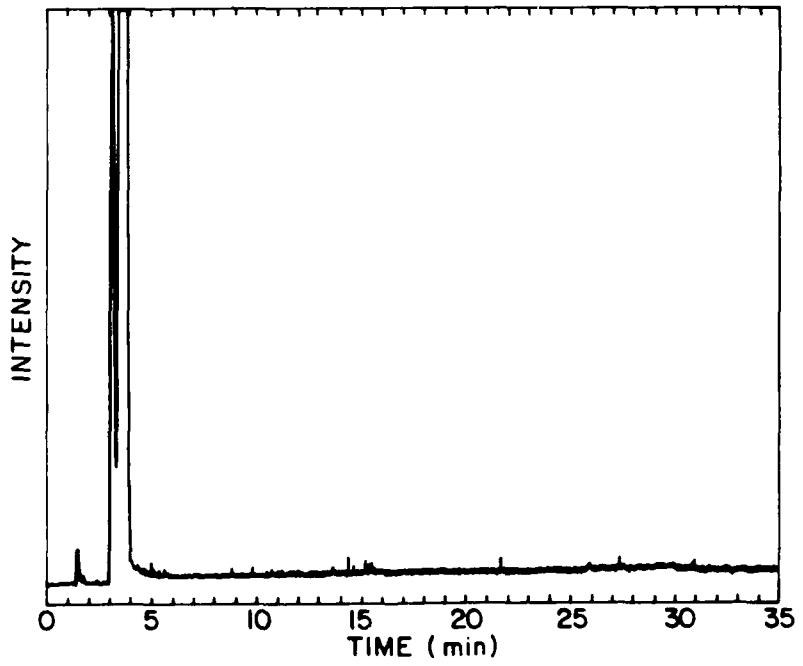



FIGURE 10: Pyrogram of polymethylmethacrylate at 800°C (flame ionization detection).

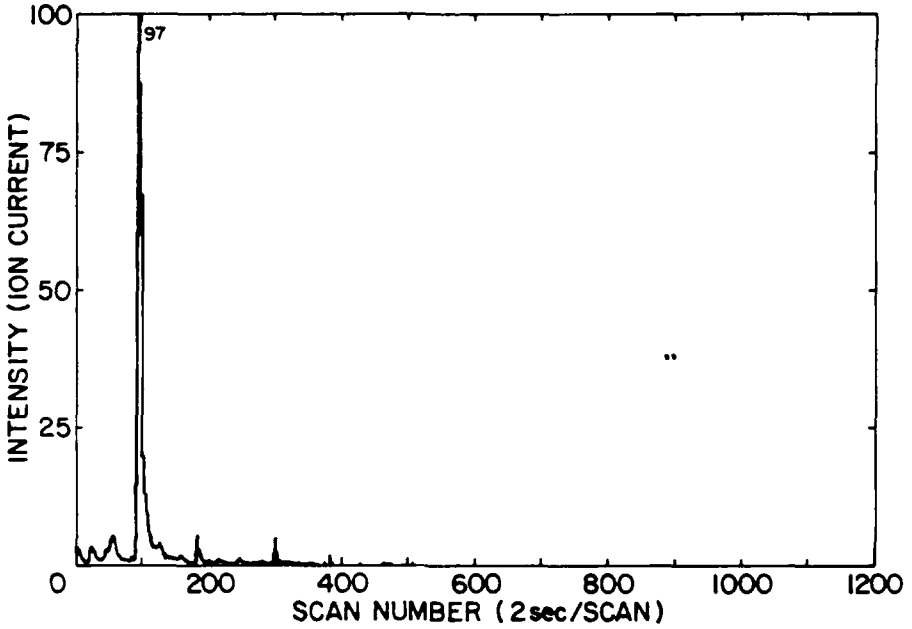



FIGURE 11: Pyrogram of polymethylmethacrylate at 1000°C (mass spectrometric detection).

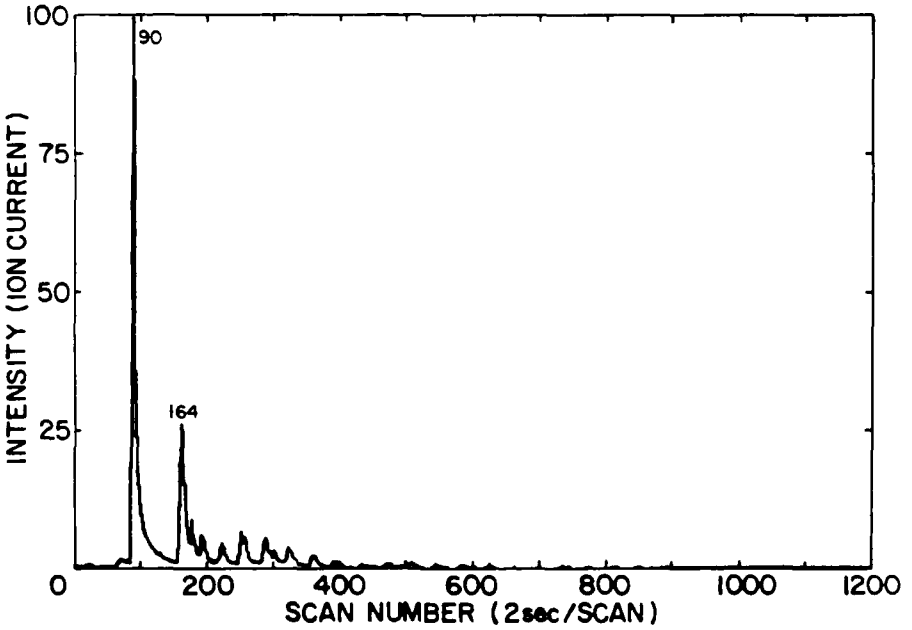



FIGURE 12: Pyrogram of polymethylmethacrylate at 800°C (mass spectrometric detection).

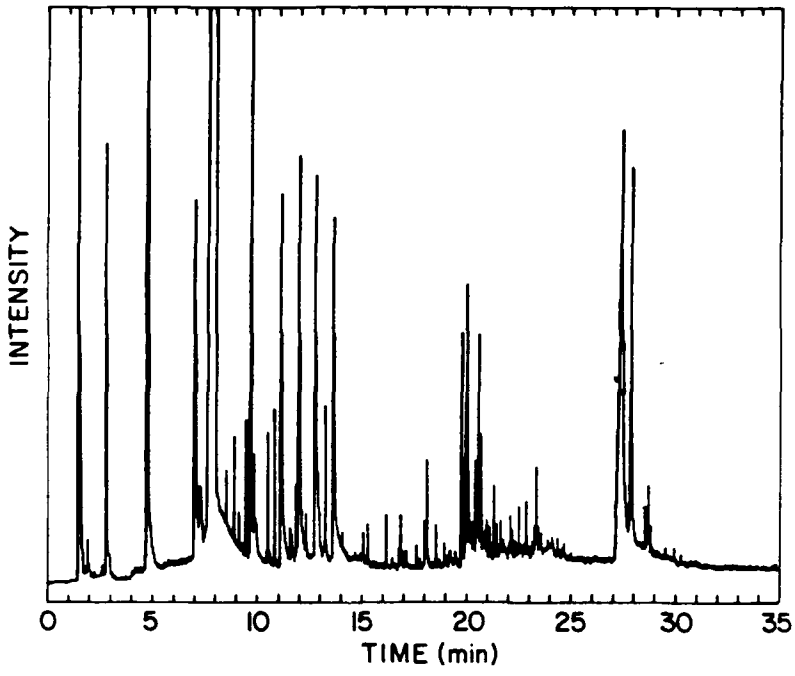



FIGURE 13: Pyrogram of polyphenylene ether at 1000°C (flame ionization detection).

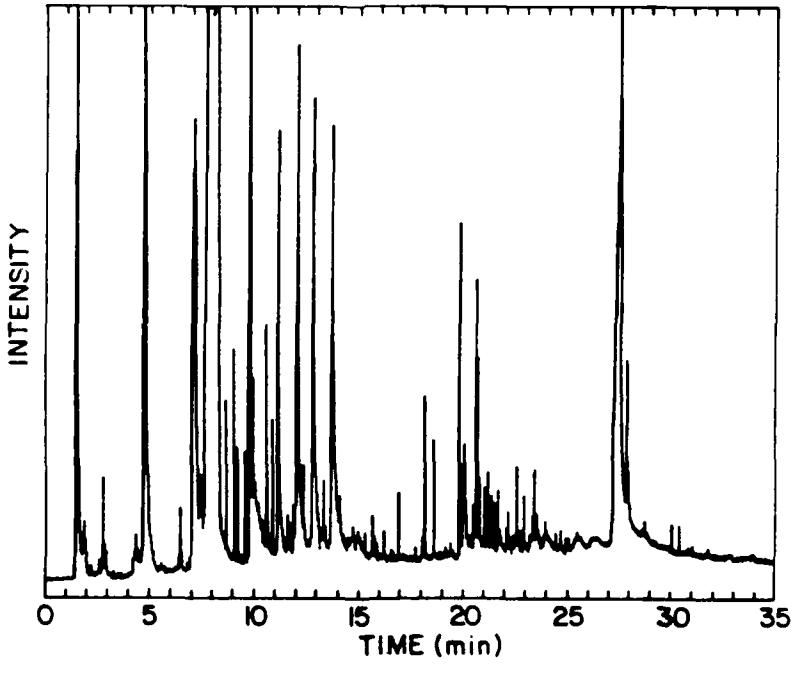



FIGURE 14: Pyrogram of polyphenylene ether at 800°C (flame ionization detection).

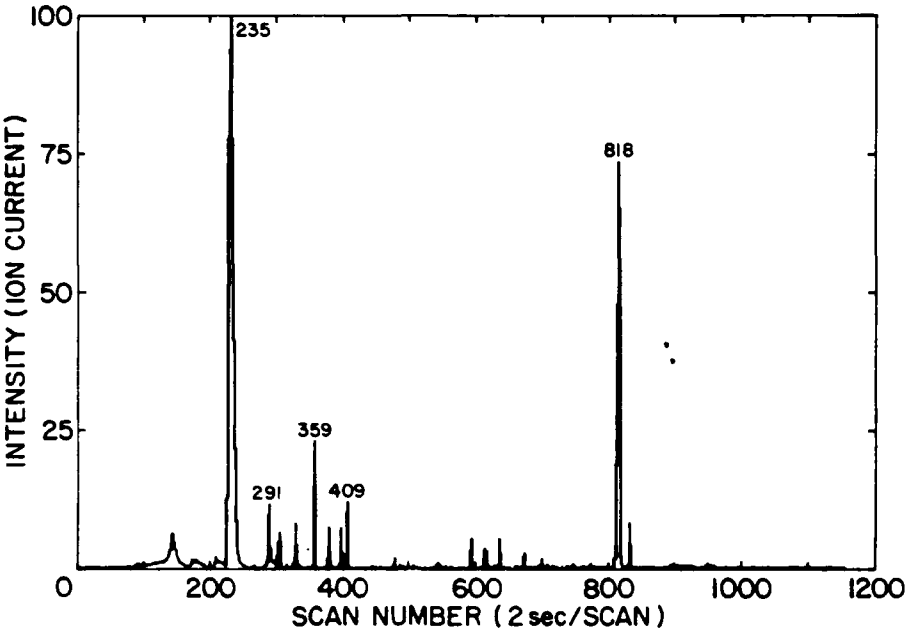



FIGURE 15: Pyrogram of polyphenylene ether at 1000°C (mass spectrometric detection).

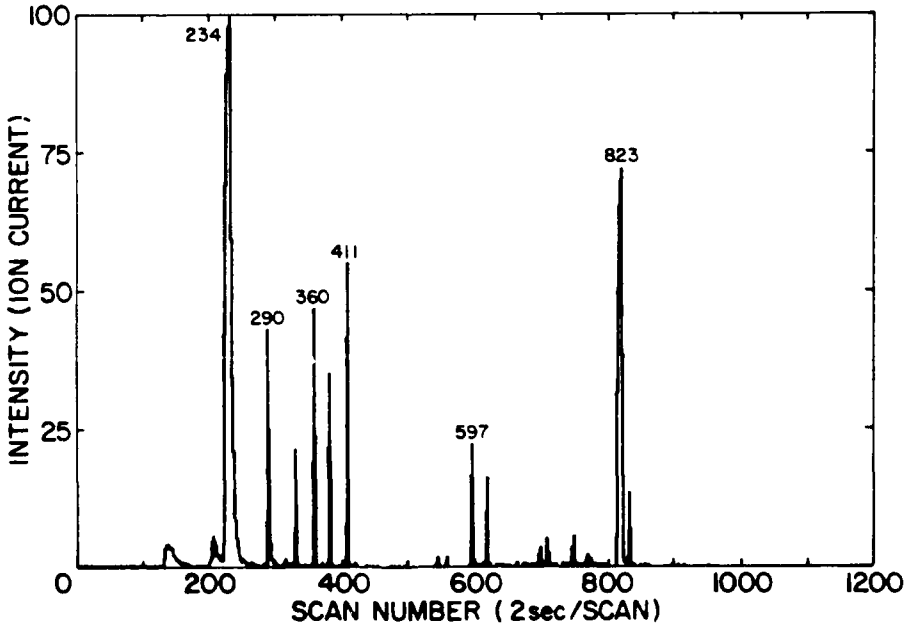



FIGURE 16: Pyrogram of polyphenylene ether at 800°C (mass spectrometric detection).

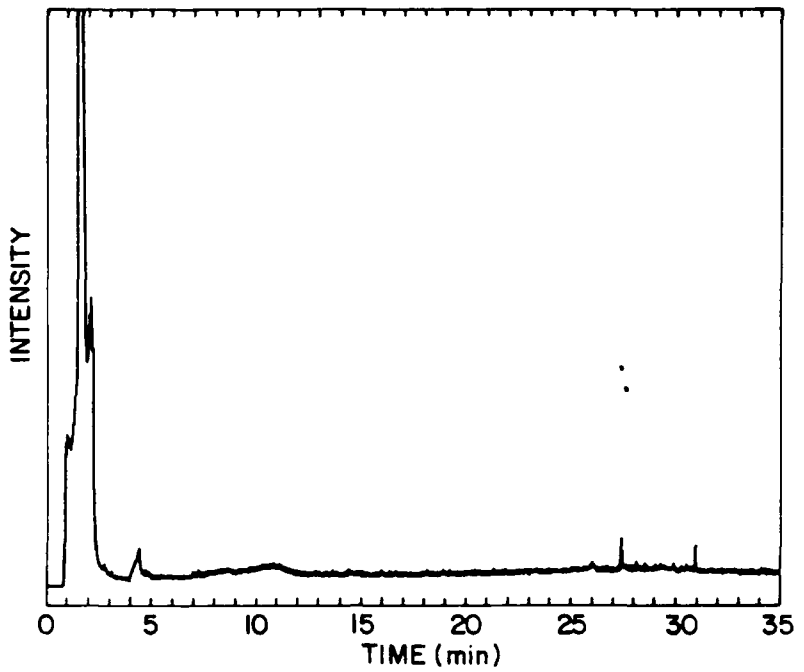



FIGURE 17: Pyrogram of polyacetal at 1000°C (flame ionization detection).

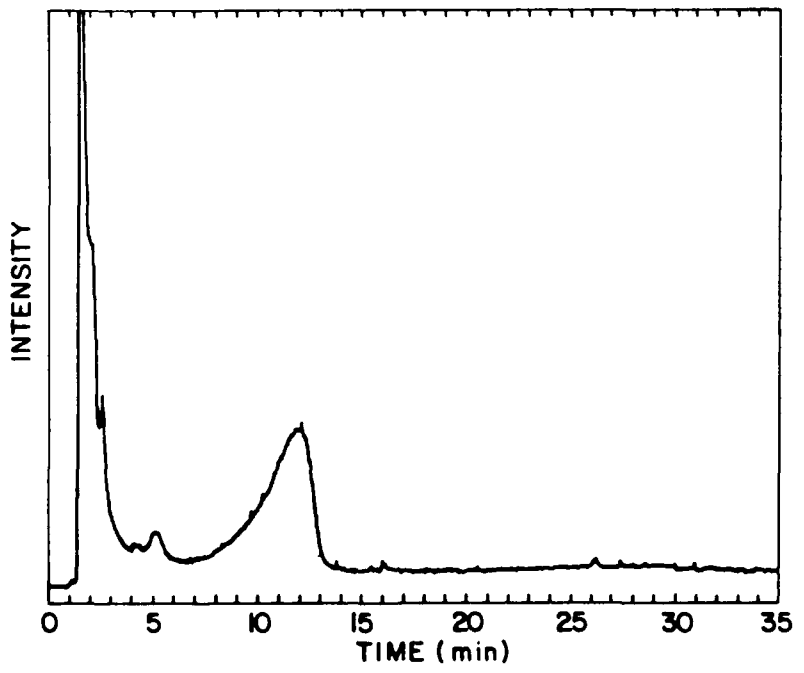



FIGURE 18: Pyrogram of polyacetal at 800°C (flame ionization detection).

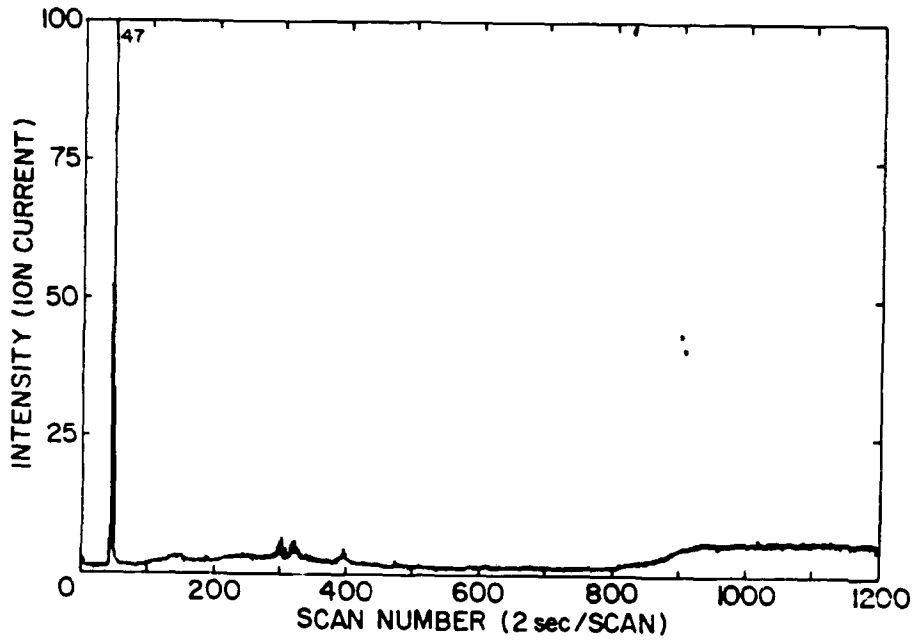



FIGURE 19: Pyrogram of polyacetal at 1000°C (mass spectrometric detection).

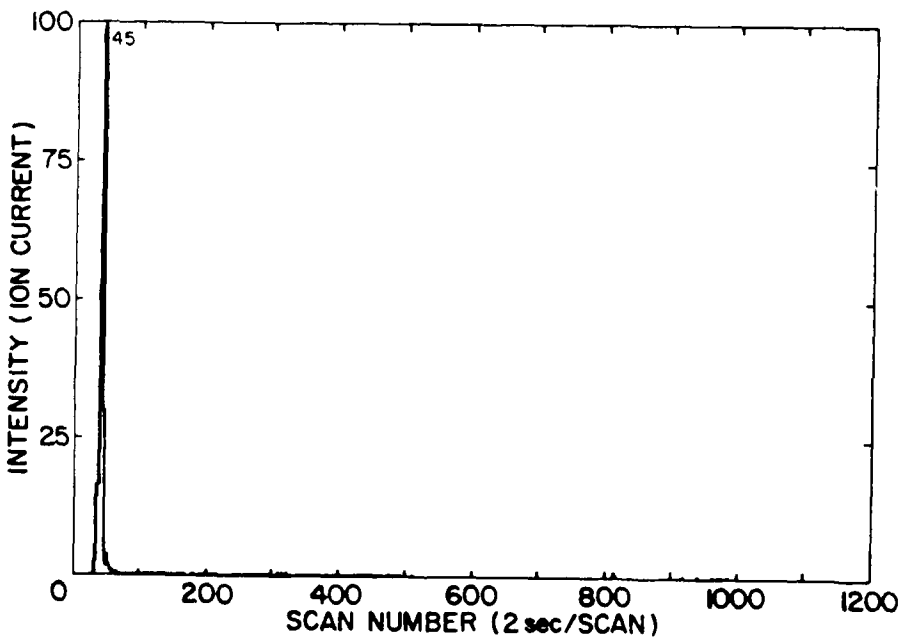



FIGURE 20: Pyrogram of polyacetal at 800°C (mass spectrometric detection).

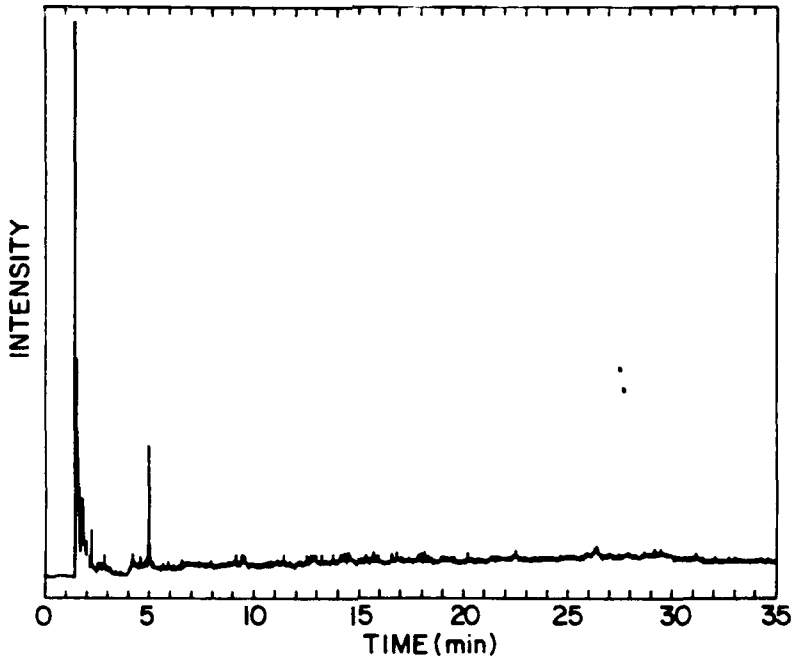



FIGURE 21: Pyrogram of Nylon 6,6 at 1000°C (flame ionization detection).

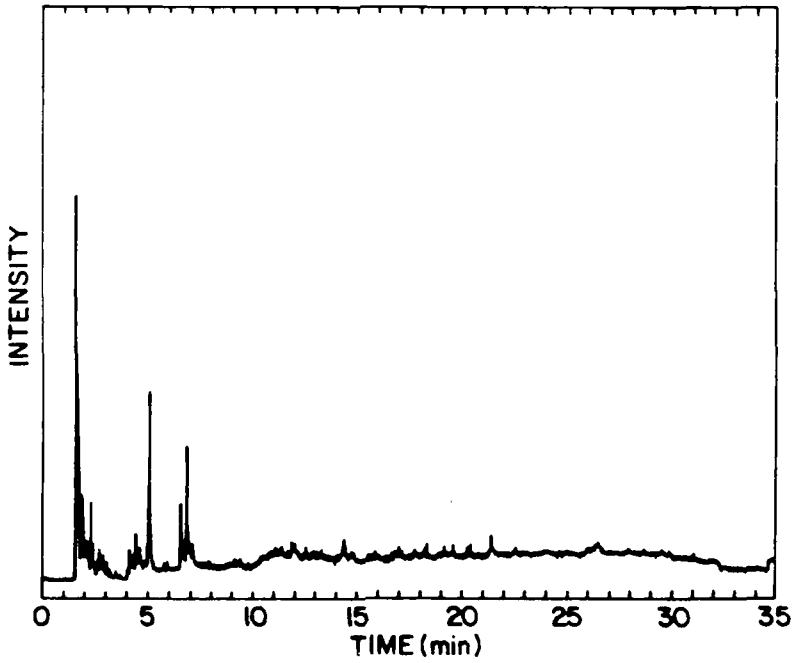



FIGURE 22: Pyrogram of Nylon 6,6 at 800°C (flame ionization detection).

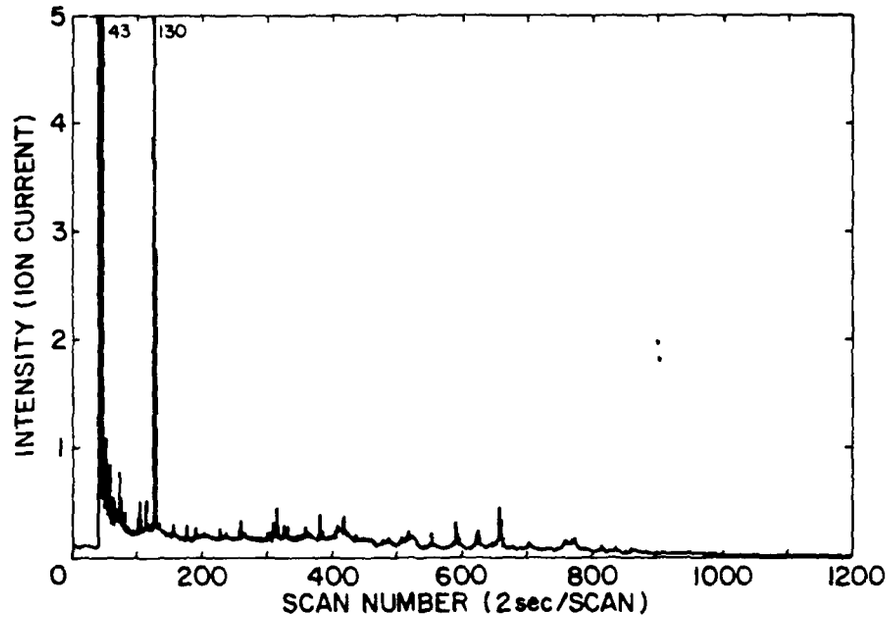



FIGURE 23: Pyrogram of Nylon 6,6 at 1000°C (mass spectrometric detection).

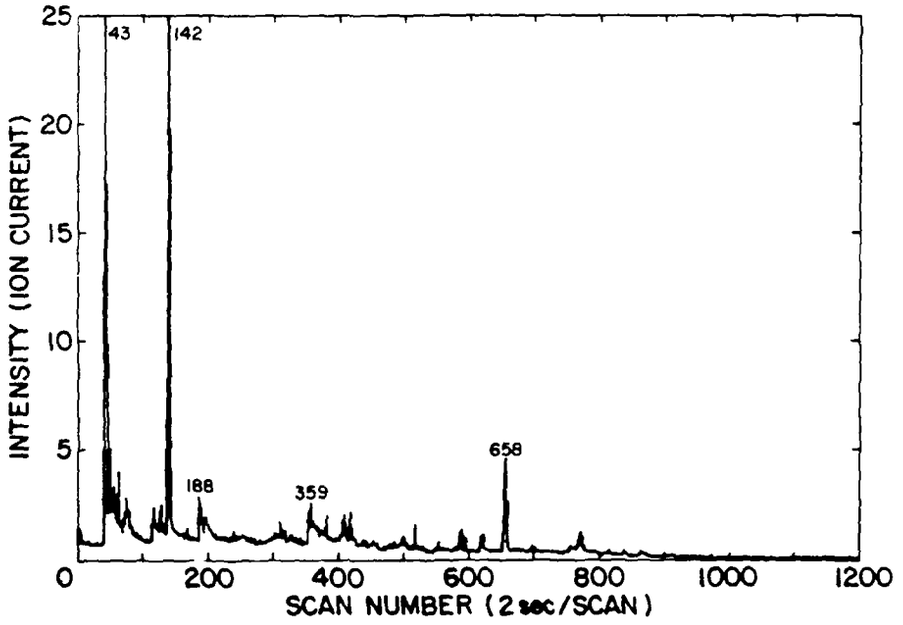



FIGURE 24: Pyrogram of Nylon 6,6 at 800°C (mass spectrometric detection).

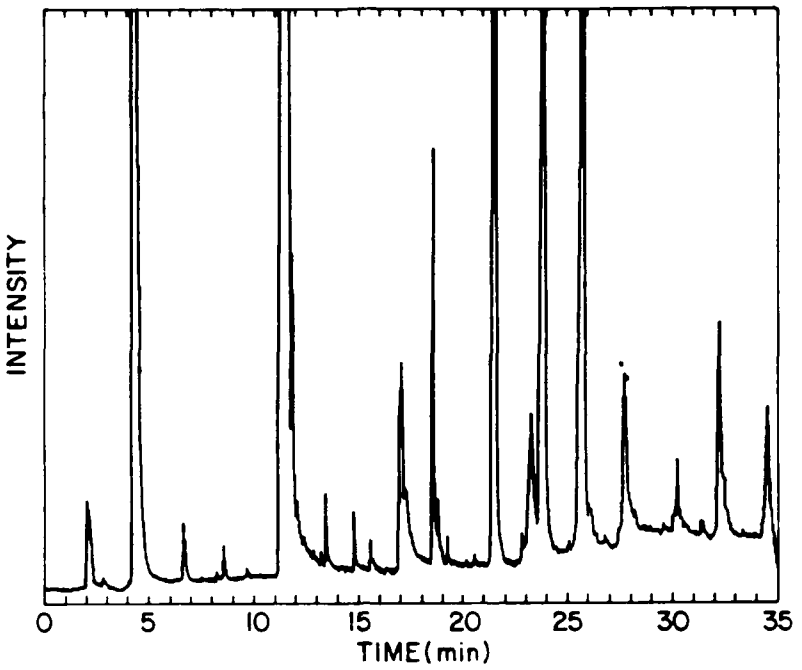



FIGURE 25: Pyrogram of polyphenylene sulfide at 1000°C (flame ionization detection).

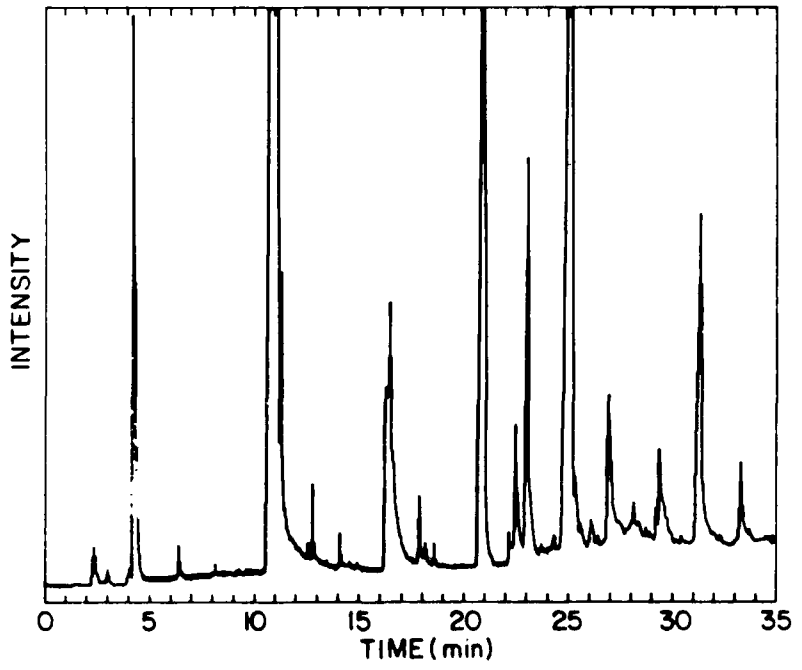



FIGURE 26: Pyrogram of polyphenylene sulfide at 800°C (flame ionization detection).

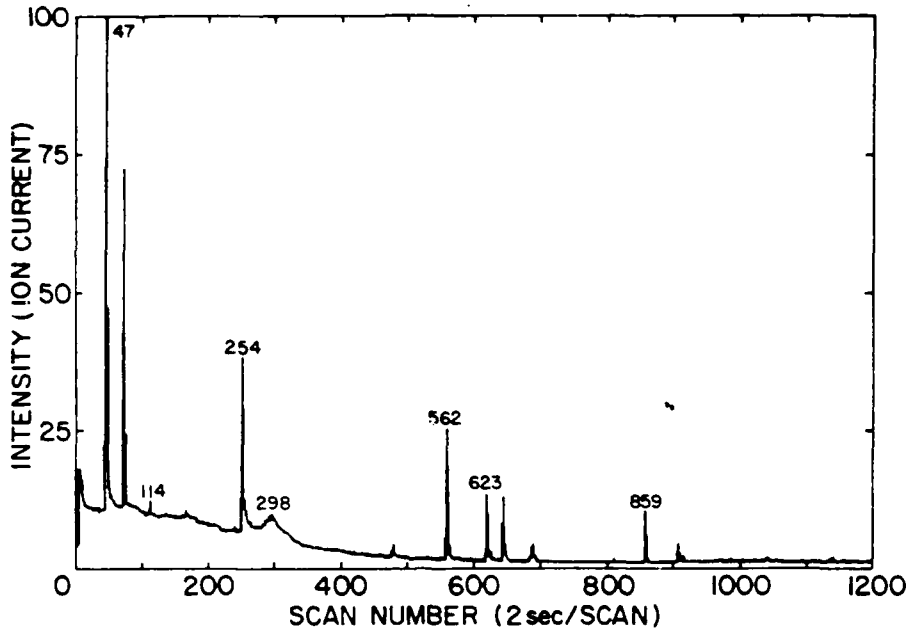



FIGURE 27: Pyrogram of polyphenylene sulfide at 1000°C (mass spectrometric detection).

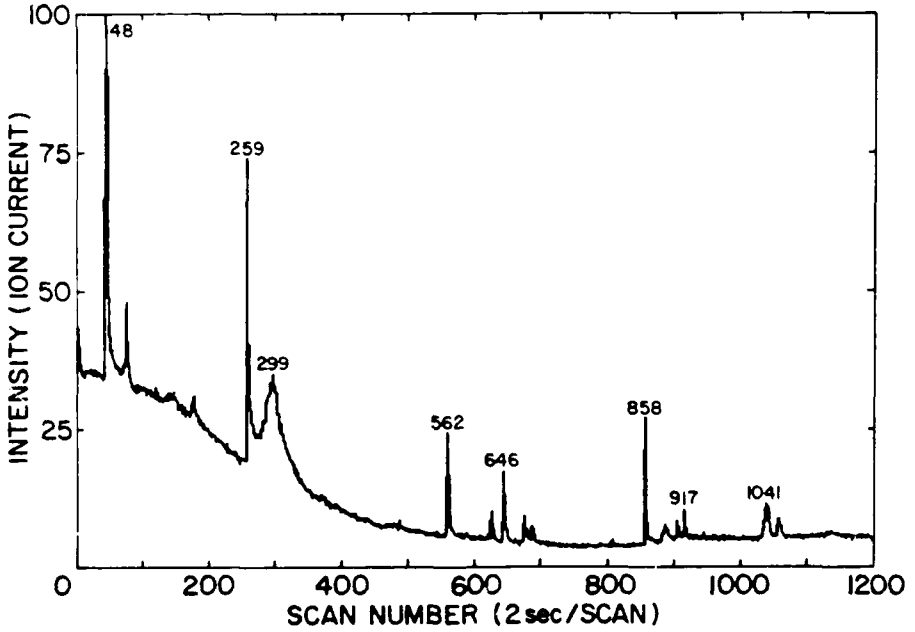



FIGURE 28: Pyrogram of polyphenylene sulfide at 800°C (mass spectrometric detection).

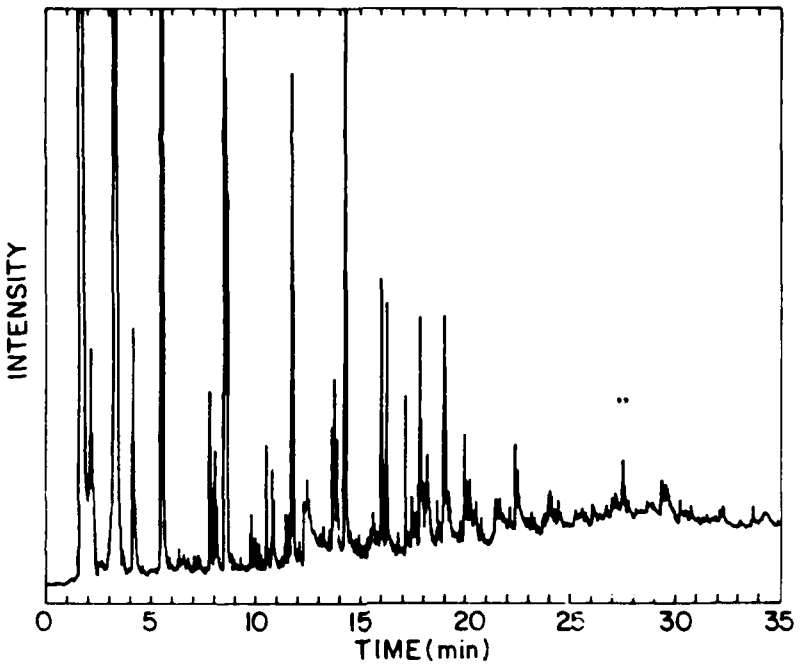



FIGURE 29: Pyrogram of polyvinylchloride at 1000°C (flame ionization detection).

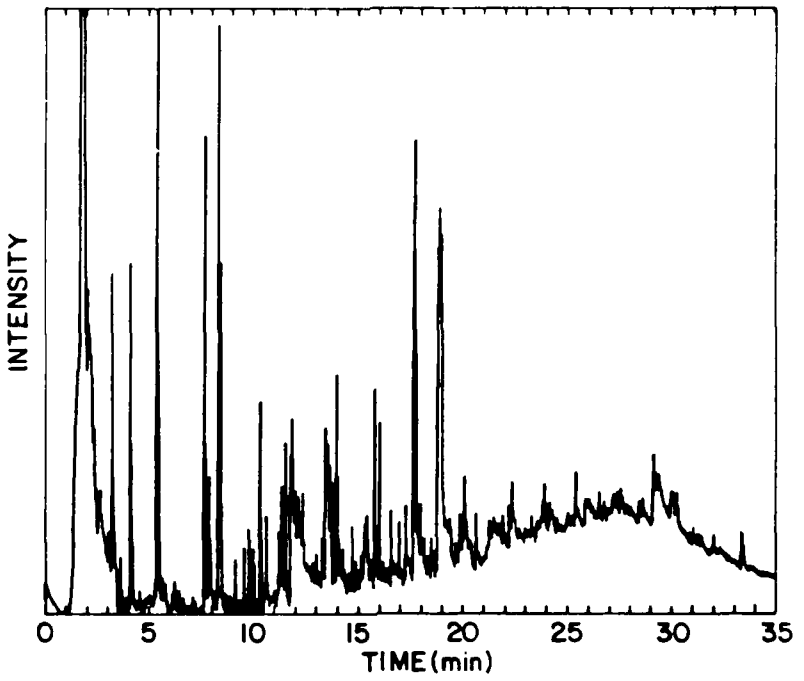



FIGURE 30: Pyrogram of polyvinylchloride at 800°C (flame ionization detection).

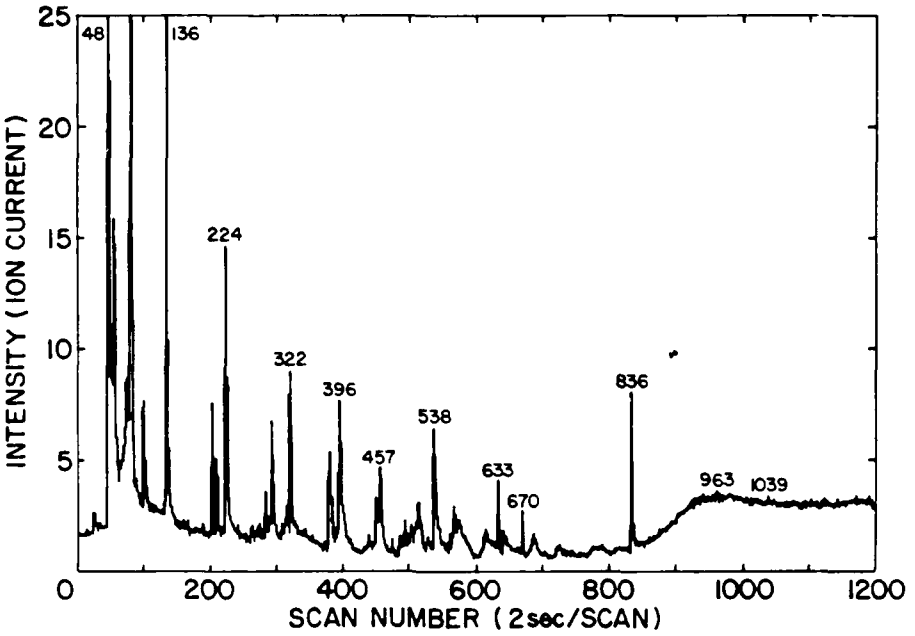



FIGURE 31: Pyrogram of polyvinylchloride at 1000°C (mass spectrometric detection).

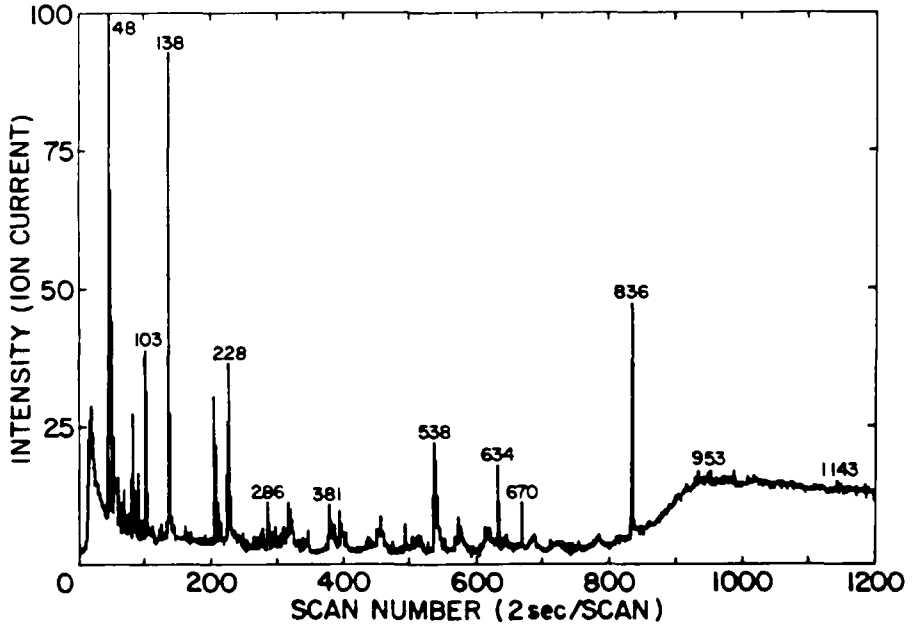



FIGURE 32: Pyrogram of polyvinylchloride at 800°C (mass spectrometric detection).

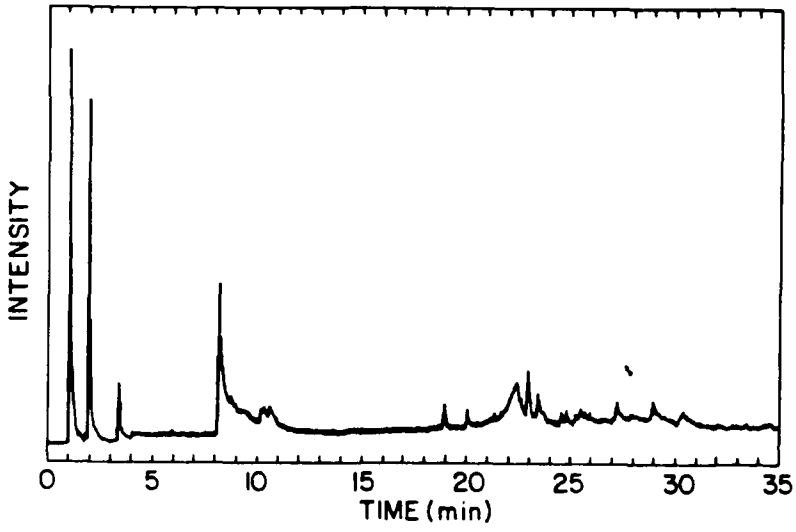



FIGURE 33: Pyrogram of polyimide at 1000°C (flame ionization detection).

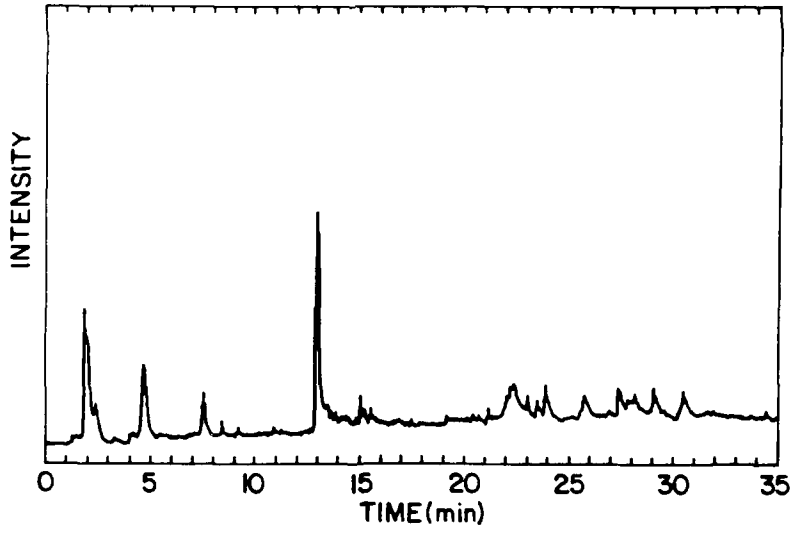



FIGURE 34: Pyrogram of polyimide at 800°C (flame ionization detection).

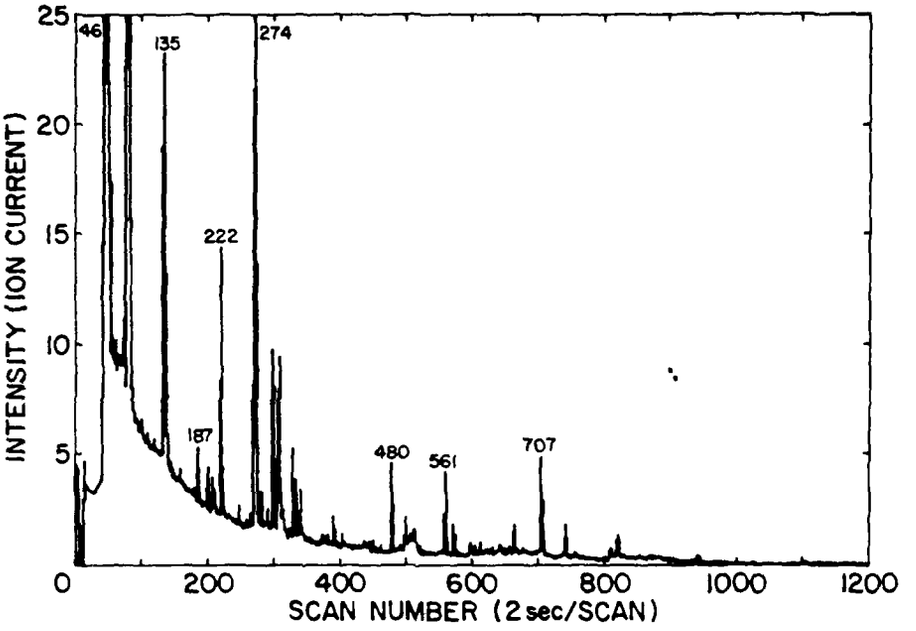



FIGURE 35: Pyrogram of polyimide at 1000°C (mass spectrometric detection).

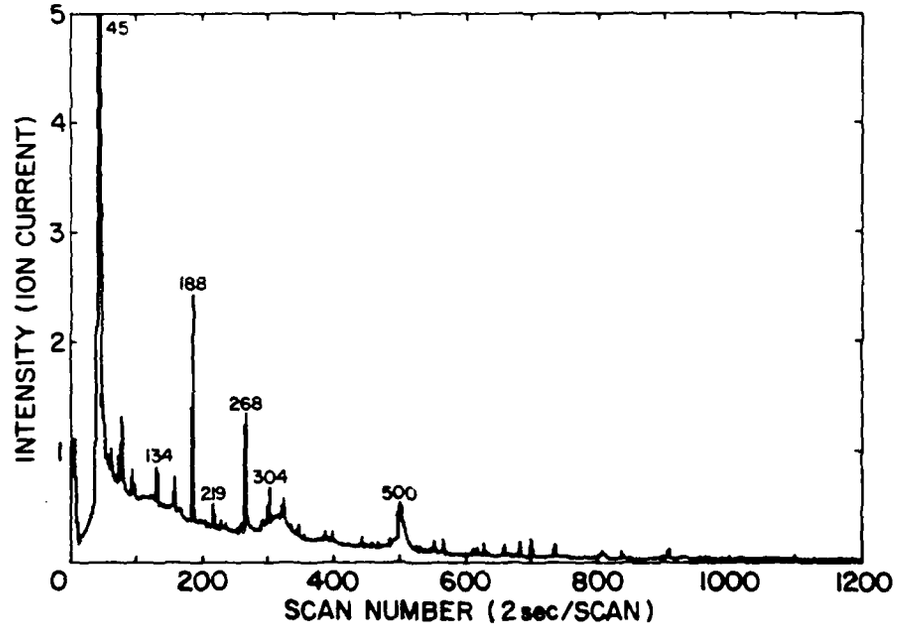



FIGURE 36: Pyrogram of polyimide at 800°C (mass spectrometric detection).

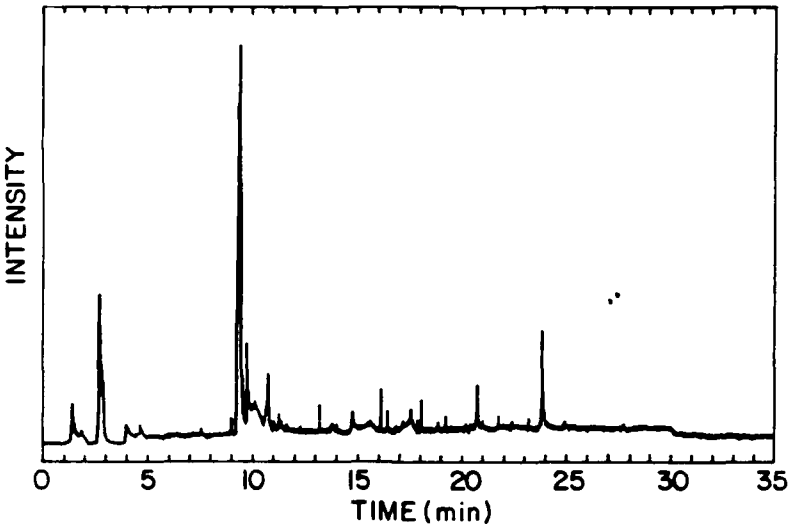



FIGURE 37: Pyrogram of polyamideimide at 1000°C (flame ionization detection).

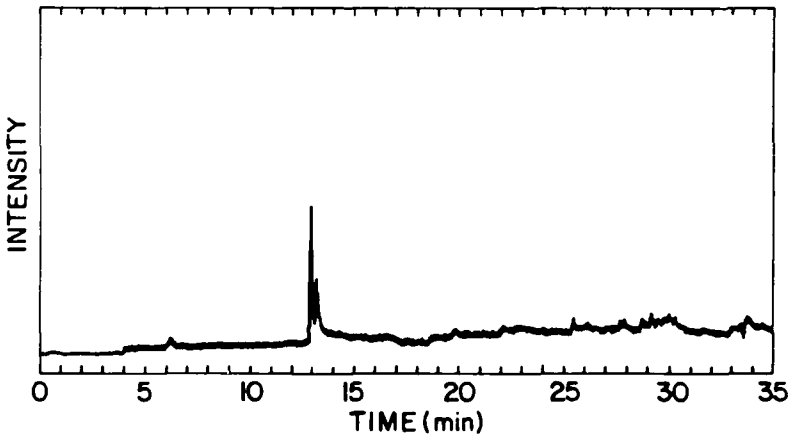



FIGURE 38: Pyrogram of polyamideimide at 800°C (flame ionization detection).

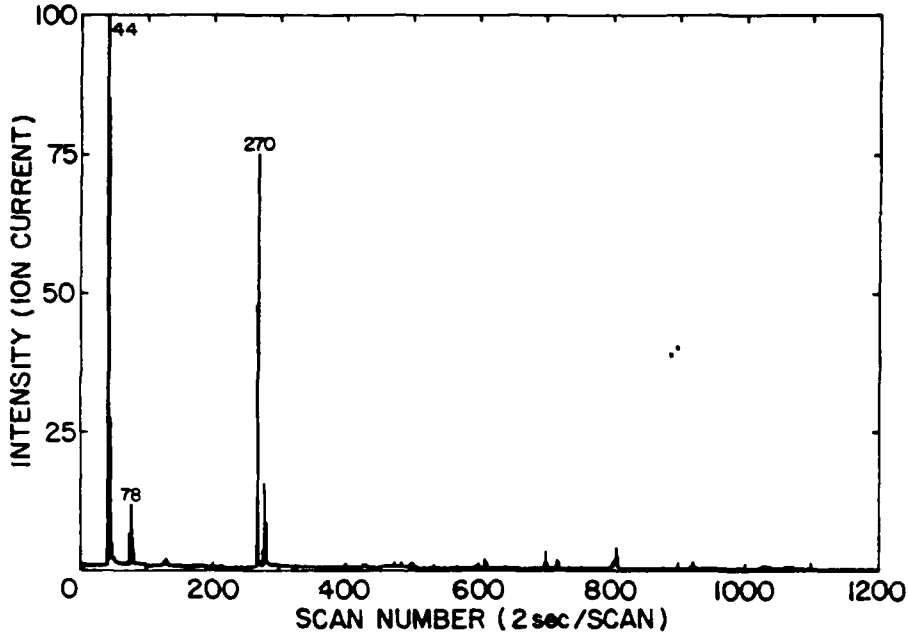



FIGURE 39: Pyrogram of polyamideimide at 1000°C (mass spectrometric detection).

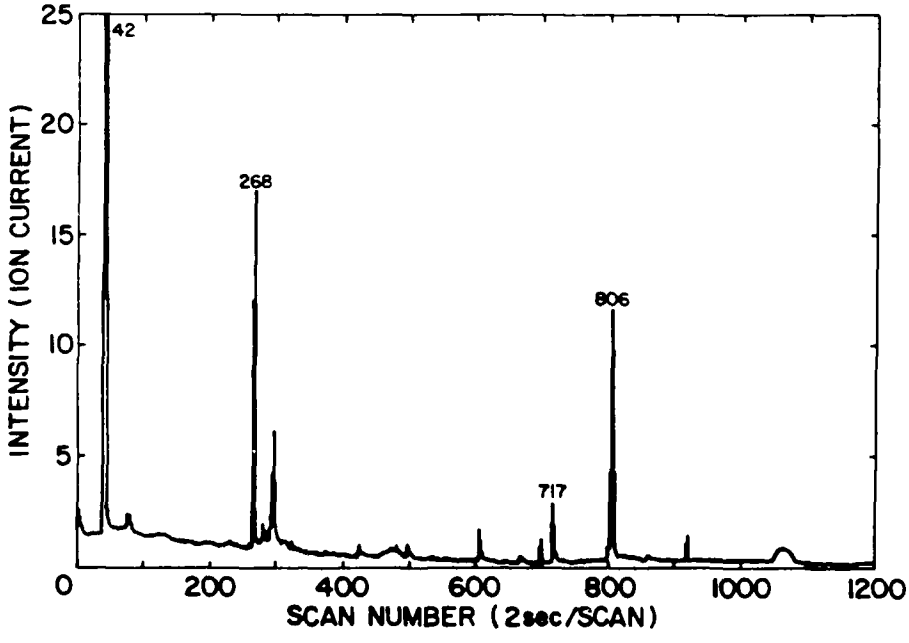



FIGURE 40: Pyrogram of polyamideimide at 800°C (mass spectrometric detection).

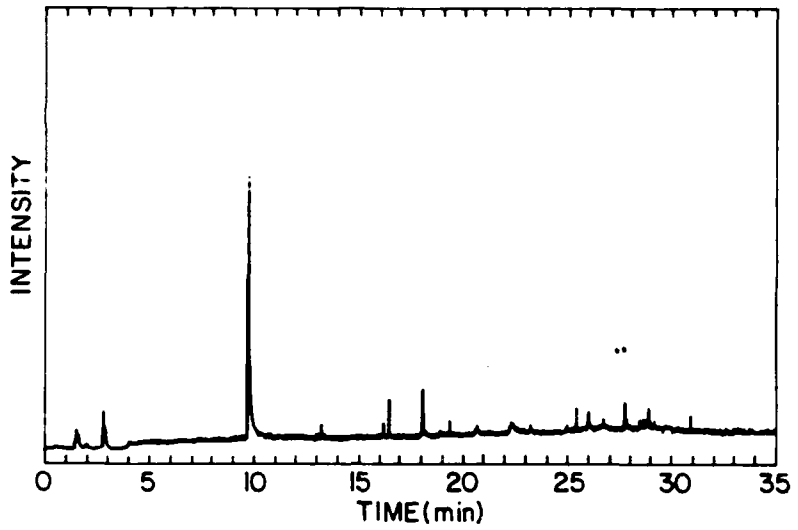



FIGURE 41: Pyrogram of polyetheretherketone at 1000°C (flame ionization detection).

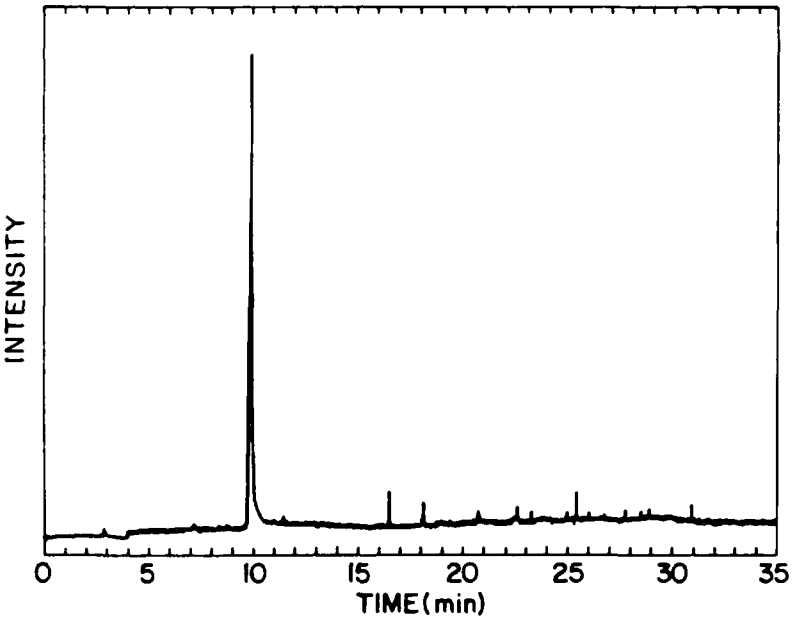



FIGURE 42: Pyrogram of polyetheretherketone at 800°C (flame ionization detection).

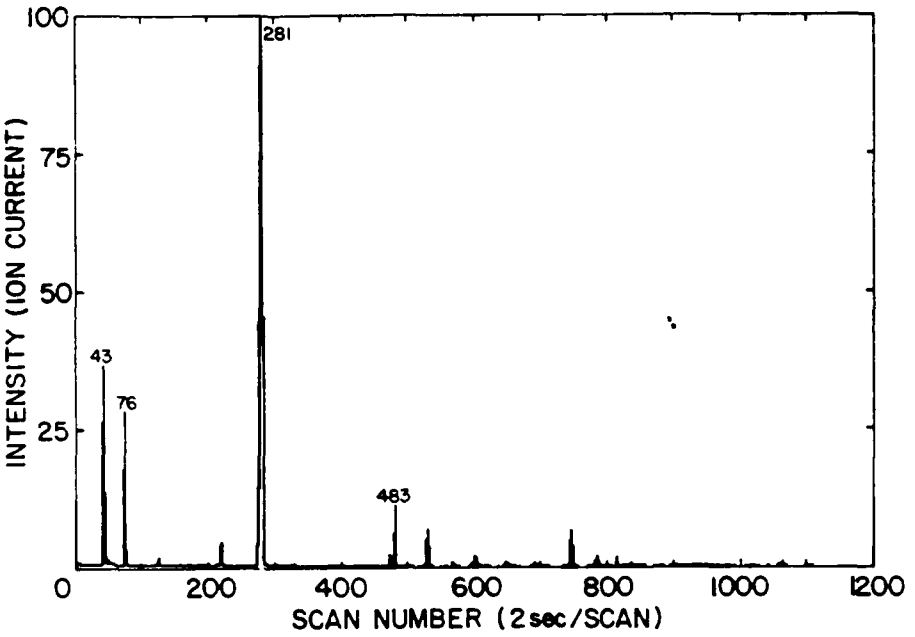



FIGURE 43: Pyrogram of polyetheretherketone at 1000°C (mass spectrometric detection).

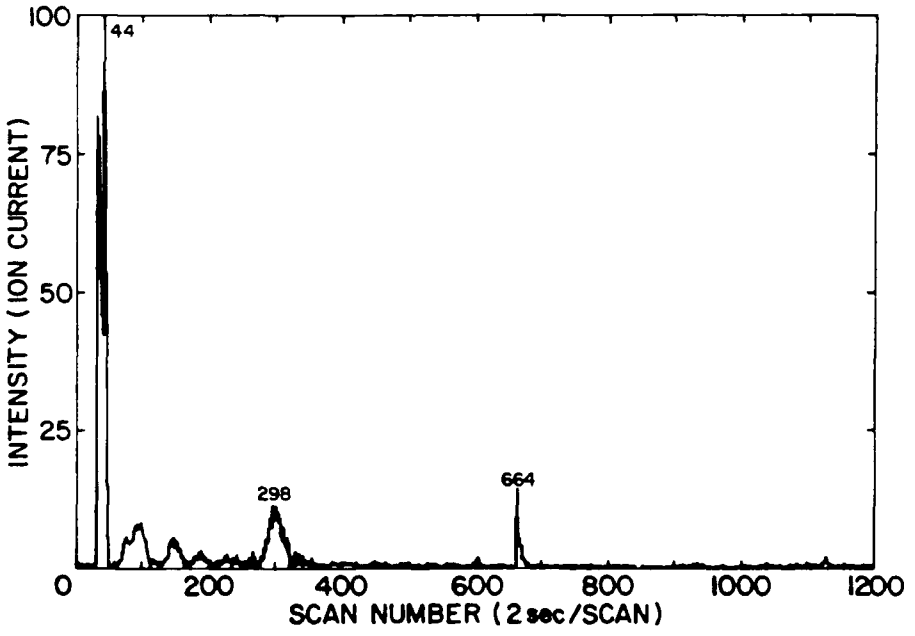



FIGURE 44: Pyrogram of polyetheretherketone at 800°C (mass spectrometric detection).

## Appendix A

Some of the pyrolysis products of the thermoplastics studied in this report. The first scan number refers to the pyrolysis at 1000°C, while the second scan number refers to the pyrolysis at 800°C.

| Compound | Scan Number | Degradation products |
|---|---|---|
| Polyethylene | | The triplets observed in the pyrograms correspond to a diene, an alkene and an alkane containing the same number of carbon atoms |
| Polymethylmethacrylate | | |
| | 97/98 | methyl ester of 2-methyl-2-propenoic acid |
| | ---*/164 | methyl ester of cyclopropane carboxylic acid |
| Polyphenylene ether | | |
| | 235/234 | styrene |
| | 291/290 | 1-methylethenylbenzene |
| | 333/332 | 2-methylphenol |
| | 359/360 | 2,5-dimethylphenol |
| | 409/411 | 2,3,6-trimethylphenol |
| | 595/597 | 1,1'-(1,3-propanediyl)bis benzene |
| | 818/823 | triphenyl ester of phosphoric acid |
| Polyacetal | | |
| | 47/45 | formaldehyde |
| Polyamide | | |
| | 43/43 | $CO_2$, propane |
| | 130/142 | cyclopentanone |
| Polyphenylene sulfide | | |
| | 47/48 | $SO_2$ |
| | 74/78 | benzene |
| | 254/259 | benzenethiol |
| | 481/483 | biphenyl |
| | 562/562 | 1,1'-thiobisbenzene |
| | 623/628 | dibenzothiophene |
| | 647/646 | S-phenyl ester of benzene-sulfinothioic acid |
| | 859/859 | 1,4-(dithiophenyl)benzene |

Appendix A (con't)

**Polyvinylchloride**

| | |
|---|---|
| 48/48 | HCl |
| 85/85 | benzene |
| 106/103 | 2-methylpropenoic acid, methyl ester |
| 136/138 | toluene |
| 209/212 | ethyl benzene |
| 224/228 | 1,3,5,7-cyclooctatetrene |
| 234/--- | dimethylbenzene |
| ---/286 | ethylmethylbenzene |
| 322/326 | 1-propynylbenzene |
| 396/400 | 1-methylene-1H-indene |

**Polyimide**

| | |
|---|---|
| 46/45 | carbon dioxide |
| 80/77 | benzene |
| 135/134 | toluene |
| 203/198 | ethylbenzene |
| 222/219 | bicyclo[4.2.0]octa-1,3,5-triene |
| 274/--- | benzonitrile |
| 324/--- | methylbenzonitrile (also 335) |
| 330/--- | methylaniline |
| 342/--- | isocyano-4-methylbenzene |
| 391/--- | naphthalene |
| 436/--- | benzenedicarbonitrile |
| 480/--- | 1,1'-biphenyl |
| 500/--- | methyl-1,1'-biphenyl |
| 561/--- | 9H-fluorene |
| 573/--- | diphenylmethanone |
| 599/--- | benzo[H]quinoline |
| 614/--- | benzo[C]cinnoline |

**Polyamideimide**

| | |
|---|---|
| 48/42 | carbon dioxide |
| 78/79 | benzene |
| 270/268 | aniline |
| 280/282 | phenol |
| 327/325 | methylaniline |
| 401/432 | benzenedicarbonitrile |
| ---/427 | benzenediamine |
| 500/500 | 1H-isoindole-1,3(2H)-dione |
| 611/608 | phenoxyaniline |
| 703/700 | phenyl-1H-isoindole-1,3(2H)-dione |
| 809/806 | 3,5-diphenyl-1,3,4-oxadiazol-2(3H)-one |

**Polyetheretherketone**

| | |
|---|---|
| 39 | carbon dioxide |
| 76 | benzene |
| 127 | toluene |
| 203 | dimethylbenzene |
| 220 | 2,5-cyclohexadiene-1,4-dione |
| 281 | phenol |
| 320 | methylphenol |
| 474 | 1,1'-biphenyl |
| 483 | 1,1'-oxybisbenzene |
| 531 | dibenzofuran |
| 568 | diphenylmethanone |
| 598 | [1,1'-biphenyl]-3-ol |
| 602 | 4-phenoxyphenol |
| 693 | (4-phenoxyphenyl)phenyl-methanone |
| 748 | 1,4-diphenoxy benzene |

*- no peak found

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